Stereocontrolled Synthesis of Carbon Chains Bearing Contiguous Methyl Groups by Iterative Boronic Ester Homologations. Application to the Total Synthesis of (+)-Faranal

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1. General Information

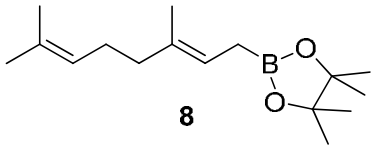
All reactions were carried out in oven dried Schlenk tubes under argon atmosphere employing standard manifold techniques. Solvents were dried by standard methods.[i] NMR spectra were recorded on JEOL 270 MHz, JEOL 400 MHz, Eclipse 300 MHz, Eclipse 400 MHz, Varian 400 MHz and Varian 500 MHz spectrometers using tetramethylsilane as the internal standard (0.00 ppm). $CDCl_3$ was used as an internal standard for ^{13}C NMR spectra (77.0 ppm). CI mass spectra were obtained using a VG Platform mass spectrometer. All IR data were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer. All MS were recorded on Agilent Technologies GC-MS Spectrum equipped with 6890 Series GC system, 7683 Series injector and 5973 Network Mass Selective detector. Analytical TLC were done on aluminium backed plates (1.5 x 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualised by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24} \bullet 4\ H_2O$ in 95% EtOH (w/v) followed by heating. Flash chromatographies were done on silica gel (Merck Kieselgel 60).

N,N,N,N-Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and (-)-sparteine was purchased from Alpha Aesar and both were distilled under reduced pressure over CaH_2 prior to use. Bis(pinacolato)diboron was purchased from AK Scientific Inc., di-μ-chlorobis[2-[(dimethylamino)methyl]phenyl-C,N]dipalladium(II) from the Aldrich Chemical Company, p-toluenesulfonic acid and dry methanol from Acros Chemical Company and were used without further purification. Dimethylsulfoxide was purchased from Aldrich and distilled over CaH_2 under reduced pressure prior to use.

2. Experimental Procedures and Data

2.1 Model synthesis from geraniol:

Procedure for the synthesis of (2*E*) 3,7-dimethyl-2,6-octadiene-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 8.[ii]



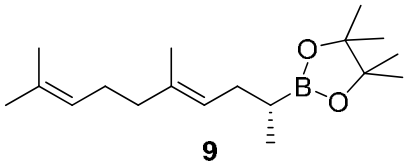
8

To a solution of geraniol (3.3 mmol) in dry DMSO (6.5 mL) and dry MeOH (6.5 mL) at room temperature was added *p*-toluenesulfonic acid (30 mg, 0.165 mmol), di-μ-chlorobis[2-[(dimethylamino)methyl]phenyl-C,N]dipalladium(II) (46 mg, 0.0825 mmol) and bis(pinacolato)diboron (1.68 g, 6.6 mmol). This mixture was then stirred at 50 °C overnight. The reaction mixture was cooled to room temperature and water (30 mL) was added, followed by Et_2O (65 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 65 mL). The combined organic layers were dried ($MgSO_4$), filtered on a thin silica pad and concentrated *in vacuo*. The crude product was purified by flash chromatography (2% Et_2O in petroleum, R_f = 0.5) to yield **8** as a colourless oil (756 mg, 87%).

IR ν_{max} (neat) / cm^{-1} 2978, 2924, 1370, 1322, 1145; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.27-5.24 (m, 1H), 5.13-5.09 (m, 1H), 2.08-1.98 (m, 4H), 1.70-1.57 (3s + m, 11H), 1.25 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) 135.1, 131.1, 124.4, 118.5, 83.0, 39.7, 26.8, 25.4, 24.7, 24.5, 17.7, 15.9; ^{11}B NMR ($CDCl_3$, 96 MHz) 35.4. Anal. Calcd for $C_{16}H_{29}BO_2$: C, 72.73; H, 11.06. Found: C, 72.39; H, 10.88. GC-MS analysis (on supelco SLB^{TM}-5ms, 15m x 0.25mm x 0.25 μm, injector 250°C, starts at 70 °C for 2 min, ramps at 25 °C/min to 150 °C, ramps at 45 °C /min to 250 °C) shows a 93:7 ratio of geometrical isomers (retention times are 6.3 (*Z*) and 6.4 minutes (*E*)); MS (EI) 278 (M^+, 3), 263 (5), 249 (10), 221 (42), 195 (20), 165(6), 149 (10), 137 (6), 121 (10), 109 (10), 102 (14), 95 (25), 83 (100), 67 (14), 55 (40).

Step by step procedures:

Procedure for the synthesis of 2*R*-(4*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-5,9-dimethyl-4,8-decadiene 9.[iii]



9

To a solution of ethyl carbamate **3** (prepared according to previous methods[iii], 440 mg, 2.5 mmol) and (-)-sparteine (580 μL, 2.5 mmol) in dry Et_2O (7 mL) at –78 °C under argon was added *s*BuLi (1.95 mL, 2.5 mmol, 1.3 M in cyclohexane) dropwise. This mixture was then stirred at –78 °C for 5 h before dropwise addition of a solution of **8** (396 mg, 1.5 mmol) in Et_2O (3 mL). The reaction was stirred for 1 h at –78 °C before addition of a solution of $MgBr_2$ [freshly made from stirring Mg turnings (92 mg, 3.8 mmol) and 1,2-dibromoethane (220 μL, 2.5 mmol) in Et_2O (5 mL) at rt for 4 h]. The reaction was stirred for a further 30 min at –78 °C, warmed to room temperature, heated to reflux and then stirred for ≥ 12 h. The reaction mixture was then cooled to room temperature and quenched with water (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 1% Et_2O/petrol) to give **9** as a pale yellow oil (342 mg, 78%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.15-5.08 (m, 2H), 2.16-1.96 (m, 6H), 1.68 (s, 3H), 1.60 (2 × s, overlapping, 2 × 3H), 1.23 (s, 12H), 1.11-1.02 (m, 1H), 0.96 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 135.1, 131.2, 124.5, 124.3, 82.8, 39.8, 31.3, 26.7, 25.7, 24.7, 17.6, 16.1, 15.1; ^{11}B NMR ($CDCl_3$, 96 MHz) δ 33.6; MS (EI) 292 (M^+, 3), 277 (3), 249 (100), 222 (2), 207 (5), 192 (6), 177 (7), 165 (10), 149 (40), 123 (85), 109 (25), 101 (87), 95 (100), 81 (65), 69 (90), 55 (45).

The e.r. of the boronic ester 9 was determined after oxidation and trapping with Mosher's acyl chloride. This sample was then compared to the racemic product (obtained by repetition of the homologation reaction with TMEDA instead of (-)-sparteine).

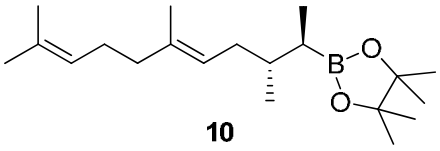
A sample of boronic ester product **9** (30 mg, 0.1 mmol) was taken up in THF (1mL) and cooled to 0 °C. A solution of NaOH (2 M)/H_2O_2 (30%) (2:1 v/v, 1.5 mL) was then

added dropwise. After stirring for 30 min at 0 °C, water (5 mL) was added and the layers were separated. The aqueous layer was then extracted with Et_2O (3 x 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*, furnishing the crude expected alcohol.

To this latter under argon in pyridine (0.5 mL) was added (S)-(+)-MTPA-Cl (28 µL, 0.15 mmol) and the mixture was stirred at room temperature for 2h. After cooling to 0 °C, water (5 mL) was added, followed by Et_2O (10 mL) and the layers were separated. The aqueous layer was then extracted with Et_2O (10 mL) and the combined organic layers were washed successively with solutions of HCl (1 N, 10 mL), 5% $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleum, R_f = 0.7) to yield the expected diastereomers as a colourless oil.

Comparison of ^{1}H NMRs of both racemic and chiral sample gave by integration of the α-methyl to the oxygen a d.r. of 96:4 (see spectra below).

Procedure for the synthesis of 2*R*,3*S*-(5*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-6,10-dimethyl-5,9-undecadiene 10.[iii]



10

To a solution of ethyl carbamate **3** (520 mg, 3.0 mmol) and (-)-sparteine (695 µL, 3.0 mmol) in dry Et_2O (15 mL) at –78 °C under argon was added *s*BuLi (2.30 mL, 3.0 mmol, 1.3 M in cyclohexane) dropwise. This mixture was then stirred at –78 °C for 5h before dropwise addition of a solution of **9** (350 mg, 1.2 mmol) in Et_2O (2.5 mL). The reaction was stirred for 1.5 h at –78 °C before addition of a solution of $MgBr_2$ [freshly made from stirring Mg turnings (110 mg, 4.5 mmol) and 1,2-dibromoethane (260 µL, 3.0 mmol) in Et_2O (6 mL) at rt for 4 h]. The reaction was stirred for a further 30 min at –78 °C, warmed to room temperature, heated to reflux and then stirred for ≥ 12h. The reaction mixture was then cooled to room temperature and quenched with water (30 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in*

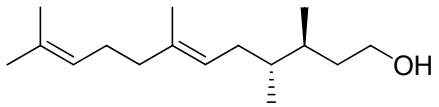
vacuo. The crude product was purified by flash chromatography (SiO_2, 1% Et_2O/petrol) to yield **10** as a pale yellow oil (199 mg, 52%).

^1H NMR ($CDCl_3$, 400 MHz) δ 5.16-5.08 (m, 2H), 2.12-1.98 (m, 6H), 1.89-1.81 (m, 1H), 1.68 (s, 3H), 1.60 (2 × s, overlapping, 2 × 3H), 1.25 (s, 12H), 1.04-0.98 (m, 1H), 0.96 (d, J = 6.3 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 135.2, 131.2, 124.5, 123.8, 82.7, 39.9, 36.6, 33.7, 26.7, 25.7, 24.8, 24.7, 18.5, 17.7, 16.1, 13.2; ^{11}B NMR ($CDCl_3$, 96 MHz) δ 33.4; MS (EI) 320 (M^+, 3), 277 (32), 197 (23), 183 (18), 167 (7), 153 (7), 139 (50), 123 (75), 101 (75), 83 (100), 69 (85), 57 (50).

The e.r. and d.r. of the boronic ester 10 were determined after oxidation and trapping with the Mosher's acyl chloride.

Procedure as for **9** (see above) gave >98:2 e.r. and 94:6 d.r. (see spectra below)

Procedure for the synthesis of 3*S*,4*R*-(6*E*)-3,4,7,11-tetramethyl-6,10-duodecadien-1-ol 12.



12

Preparation of vinyllithium solution:[iv] ^{n}BuLi (2.5 M in hexanes, 320 μL, 0.8 mmol) was added dropwise at room temperature to tetravinyltin (73 μL, 0.4 mmol) in a flame dried Schlenk tube under argon. After stirring for 30 minutes, the liquid was removed by cannula and the white solid was washed with dry pentane (4 x 350 μL). The remaining solid was diluted in THF (230 μL) and the solution was titrated (~ 2.8 M).

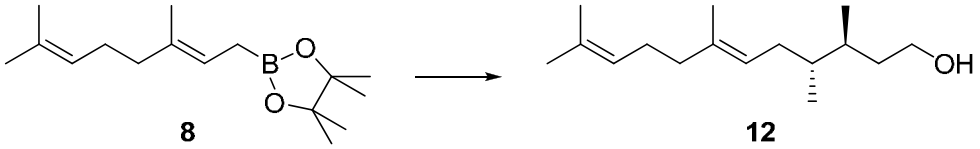
To a solution of boronic ester **10** (130 mg, 0.43 mmol) in Et_2O (1 mL) at –78 °C under argon was added a freshly made solution of vinyllithium (230 μL, 0.65 mmol, ~ 2.8 M in THF) dropwise. After stirring for 45 minutes at –78 °C, a solution of I_2 (164 mg, 0.65 mmol) in MeOH (4 mL) was added, followed 15 minutes later by a solution of MeONa (70 mg, 1.30 mmol) in MeOH (1.3 mL). The mixture was then allowed to stir at room temperature for 1 h and concentrated. The crude was taken up into Et_2O (25 mL) and washed successively with 5% NaS_2O_3 solution, 5% NaOH solution, 5% NaOH solution containing 10% H_2O_2, 5% NaS_2O_3 solution again and finally brine. The ethereal layer was then dried ($MgSO_4$) and concentrated *in vacuo*.

To this crude triene **11** in Et_2O (3 mL) at 0 °C under argon was added a 0.5 M solution of 9-BBN (made from 105 mg of dimer, 0.43 mmol in 1.7 mL of THF). The cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 2.5 h. The mixture was then cooled to 0 °C and a pre-mixed solution of NaOH (2 M) / H_2O_2 (30%) (2:1 v/v, 6.0 mL) was added. After 30 minutes, the mixture was poured onto $NaHCO_3$ sat. solution (10 mL) and extracted with Et_2O (15 mL). The aqueous layer was extracted with Et_2O (2 x 10 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 33% Et_2O in petrol, R_f = 0.3) to yield **12** as a yellow oil (78 mg, 76 %). All spectral data were in accordance with literature values.[xv]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.15-5.07 (m, 2H), 3.80-3.59 (m,2H), 2.13-1.96 (m, 6H), 1.90-1.30 (m, 4H), 1.69 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.20-1.17 (m, 1H, OH), 0.89 (d, J = 7.0 Hz, 3H), 0.83 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 135.3, 131.3, 124.4, 123.9, 61.2, 39.8, 38.7, 35.9, 33.6, 31.5, 26.6, 25.7, 17.7, 16.7, 16.1, 16.0; MS (EI) 238 (M^+, 3), 195 (10), 177 (4), 165 (2), 137 (5), 123 (35), 109 (25), 99 (17), 95 (15), 83 (37), 81 (37), 69 (100), 55 (50); $[\alpha]^{23}_D$ = - 4.8 (*c* 4.20, $CHCl_3$) (d.r. = 94:6), Lit.[xv]: $[\alpha]^{23}_D$ = - 4.6 (*c* 4.21, $CHCl_3$) (d.r. = 94:6).

<u>One-pot procedure:</u>

Procedure for the synthesis of 3*S*,4*R*-(6*E*)-3,4,7,11-tetramethyl-6,10-duodecadien-1-ol 12.



8 **12**

To a solution of ethyl carbamate **3** (260 mg, 1.5 mmol) and (-)-sparteine (340 µL, 1.5 mmol) in dry Et_2O (7.5 mL) at –78 °C under argon was added *s*BuLi (1.15 mL, 1.5 mmol, 1.3 M in cyclohexane) dropwise. This mixture was then stirred at –78 °C for 5h before addition of **8** (264 mg, 1.0 mmol) in Et_2O (2 mL) dropwise. The reaction was stirred for a further hour at –78 °C before addition of a freshly made solution of $MgBr_2$ (from stirring Mg turnings (60 mg, 2.5 mmol) and 1,2-dibromoethane (130 µL, 1.57 mmol) in Et_2O (3. mL) at room temperature for 4 h). The reaction was stirred for a further 30 min at –78 °C, warmed to room temperature, heated to reflux and then stirred for ≥ 12 h.

The reaction mixture was cooled to room temperature and the crude boronic ester **9** just obtained was then added at – 78 °C to a second solution of freshly made lithiated carbamate **3** (1.5 mmol, as above). After stirring for 30 min at -78 °C, a freshly made solution of $MgBr_2$ was added (2.5 mmol, as above) and the reaction mixture heated to reflux for ≥ 12 h.

The crude mixture of **10** was cooled to room temperature and then to -78 °C before addition of a freshly made vinyllithium solution (1.8 mL, 5.0 mmol, ~ 2.8 M, see below).

Preparation of vinyllithium solution[iv]: ^{n}BuLi (2.5 M in hexanes, 3.8 mL, 6.0 mmol) was added dropwise at room temperature to tetravinyltin (550 µL, 3.0 mmol) in a flame dried Schlenk tube under argon. After stirring for 30 minutes, the liquid was removed by cannula and the white solid was washed with dry pentane (4 x 2 mL). The remaining solid was diluted in THF (1.8 mL) and the solution was titrated (~ 2.8 M).

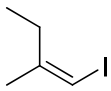
After stirring the mixture for an additional 45 minutes at -78 °C, a solution of I_2 (1.27 g, 5.0 mmol) in MeOH (28 mL) was added, followed 30 minutes later by a solution of MeONa (580 mg, 10.0 mmol) in MeOH (10 mL). The mixture was then allowed to stir at room temperature for 1 h and concentrated. The crude was taken up into Et_2O (130 mL) and washed successively with 5% NaS_2O_3 solution, 5% NaOH solution, 5% NaOH solution containing 10% H_2O_2, 5% NaS_2O_3 solution again and finally brine. The ethereal layer was then dried ($MgSO_4$) and concentrated *in vacuo*.

To the crude triene **11** in Et_2O (8 mL) at 0 °C under argon was added a 0.5 M solution of 9-BBN (made from 366 mg of dimer, 1.5 mmol, in 6.0 mL of THF). The cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 2.5 h. The mixture was then cooled to 0 °C and a pre-mixed solution of NaOH (2 M) / H_2O_2 (30%) (2:1 v/v, 12.0 mL) was added. After 30 minutes, the mixture was poured onto $NaHCO_3$ sat. solution (50 mL) and extracted with Et_2O (75 mL). The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 20% Et_2O in petrol, R_f = 0.3) to yield **12** as a yellow oil (143 mg, 60%, d.r. = 94:6, see spectra below).

Analytical data: see above.

2.2 Faranal synthesis:

Procedure for the synthesis of (*Z*) 1-iodo-2-methyl-1-butene 18.[v]

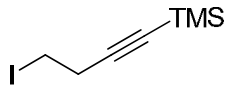


18

To a slurry of dichlorobis[η^5-cyclopentadienyl]zirconium (14.6 g, 50 mmol) in DCM (125 mL) under argon was added triethylaluminium solution (100 mL, 100 mmol, 1M in hexanes) at 0 °C and the mixture was stirred for 5 minutes. To this solution was added freshly condensed propyne (2.7 mL, 50 mmol) in DCM (2 mL) and the reaction mixture was stirred for 30 minutes at 0 °C and then warmed to RT. After stirring the solution for 40 h, a solution of iodine (19.2 g, 75 mmol) in THF (115 mL) was added dropwise at 0 °C and the mixture stirred for 40 h from 0 °C to room temperature. The reaction was then quenched by careful addition of 50 mL of water at 0 °C. The resulting mixture was filtered and the solids washed with Et_2O. The organic layer was separated and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were washed with $Na_2S_2O_3$ solution (5%), dried over magnesium sulfate and the solvents were distilled at atm. pressure. The remaining oil was then distilled under vacuum (1 mm Hg, 36-45 °C) affording the iodine **18** (7.0 g, 72%) as a yellow liquid. Spectra were in accordance with published data.[vi]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.79 d (d, *J* = 1.1 Hz, 1H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.89 (d, *J* = 1.1 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 149.0, 73.0, 32.0, 22.7, 11.4.

Procedure for the synthesis of 4-iodo-1-trimethylsilylbutyne 19.[vii]



19

A solution of TsCl (11 g, 57.7 mmol) in 50 mL CH_2Cl_2 was added to the 250 mL flask containing a solution of 3-butyn-1-ol (4 g, 57 mmol) and NEt_3 (11.5 g, 114 mmol) in 50 mL CH_2Cl_2 at 0 ºC. The mixture was stirred at room temperature for 2 h and then poured into 60 mL ice/H_2O. The aqueous layer was separated and extracted with CH_2Cl_2 (50 mL x 2). The combined organic extracts were washed with NH_4Cl (aq.), $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated.

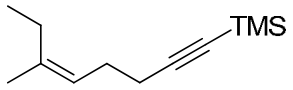
The crude tosylate was dissolved in 80 mL dry THF and cooled to -78 ºC, to which ^{n}BuLi (25 mL, 2.5 M in hexanes, 62.4 mmol) was slowly added. The mixture was stirred at -78 ºC for 1 h. To this dark brownish solution was added TMSCl (8 g, 73.6 mmol). The resulting mixture was warmed up to r.t. over 2 h and then poured into 100 mL ice/H_2O. The residue was extracted with EtOAc (200 mL x 2 + 50 mL). The combined organic extracts were washed with NH_4Cl (aq.) and brine, dried over $MgSO_4$ and concentrated.

The crude compound was then dissolved in 50 mL acetone, to which NaI (17 g, 115 mmol) was added. The mixture was stirred at r.t. overnight and diluted with 150 mL H_2O. The residue was extracted with pentane (100 mL x 4). The combined organic extracts were washed with $NaHCO_3$ (aq.) and brine, dried over $MgSO_4$ and concentrated by the rotary evaporation. The crude product was purified by flash chromatography (petrol, R_f = 0.5) affording the iodine **19** (10.4 g, 72%) as a colourless liquid.

All spectral data were in accordance with literature values.[viii]

IR ν_{max} (neat) / cm^{-1} 2959, 2176, 1248, 1171, 837, 758, 652; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 2H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 105.0, 86.8, 25.0, 1.0, -0.1.

Procedure for the synthesis of (*Z*) 1-trimethylsilyl-6-methyl-oct-5-en-1-yne 20.[viii]



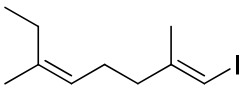
20

A solution of the iodide **19** (3.6 g, 14.1 mmol) in diethyl ether (28 mL) was added dropwise *via* cannula over 15 minutes to a stirred solution of *tert*butyllithium (1.5 M in pentane, 19 mL, 28.3 mmol) in diethylether (40 mL) at -78 ºC under argon. The solution was stirred at -78 ºC for 90 minutes and then a solution of anhydrous zinc bromide (4.2 g, 18.9 mmol, pre-dried by heating at 150 ºC under reduced pressure [~0.1 Torr] for ≥5 h), in THF (38 mL) was added dropwise *via* cannula over 5 minutes. The mixture was allowed to warm to 0 ºC over 1 h and then added dropwise *via* cannula over 5 minutes to a stirred mixture of *tetrakis*(triphenylphosphine)-palladium (0.4 g, 0.4 mmol) and vinyl iodide **18** (1.86 g, 9.4 mmol) at 0 ºC. The mixture was allowed to warm to room temperature over 16 h and then quenched with

water (70 mL). The separated aqueous phase was extracted with diethylether (3 × 70 mL) and the combined organic extracts were then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (nearly filtration to avoid degradation, ~ 15 minutes) (petrol, R_f = 0.6) affording the not entirely pure en-yne **20** (1.8 g, 97%) as a pale yellow liquid. This was used without further purification. All spectral data were in accordance with literature values.[ix]

IR ν_{max} (neat) / cm^{-1} 2963, 2176, 1249, 1040, 828, 758; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.11 (bt, *J* = 7.8 Hz, 1H), 2.25-2.22 (m, 4H), 2.05 (q, *J* = 7.5 Hz, 2H), 1.70 (d, *J* = 1.1 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 138.7, 122.3, 107.4, 84.3, 27.1, 24.8, 22.9, 20.6, 12.9, 0.1.

Procedure for the synthesis of (1E,5Z)-1-iodo-2,6-dimethylocta-1,5-diene 21 (without isolation of intermediate terminal alkyne 6).



21

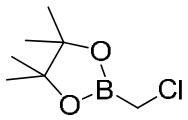
Deprotection - A mixture of silyl derivative **20** (3.21 g, 16.5 mmol), K_2CO_3 (6.85 g, 50.0 mmol) and MeOH (200 ml) was stirred at RT under N_2 for 5 h. Water (100 ml) was then added and the reaction extracted with pentane (3 × 75 ml). The organics were combined and dried over $MgSO_4$. The solution was then concentrated (to ~10 ml) by careful removal of solvent at -20 °C under reduced pressure (~20 Torr). The solution (under argon) was used directly (see below).

Carboalumination[v] - To a slurry of dichlorobis[η^5-cyclopentadienyl]zirconium (4.80 g, 16.5 mmol) in DCM (40 mL) under argon was added trimethylaluminium solution (16.5 mL, 33.0 mmol, 2M in hexanes) at 0 °C and the mixture was stirred for 5 minutes. To this solution was added the solution of alkyne **6** (see above) and the reaction mixture was stirred for 30 minutes at 0 °C and then warmed to RT. After stirring the solution for 40 h, a solution of iodine (6.3 g, 24.8 mmol) in THF (40 mL) was added dropwise at 0 °C and the mixture stirred for 40 h from 0 °C to room temperature. The reaction was then quenched by careful addition of 50 mL of water at 0 °C. The resulting mixture was filtered and the solids washed with Et_2O. The organic layer was separated and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were washed with $Na_2S_2O_3$ solution (5%), dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash chromatography (petrol, R_f = 0.5) affording the not entirely pure iodide **21** (2.7 g, 62%) as a colourless liquid.

All spectral data were in accordance with literature values.[x,xi]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88 (d, *J* = 1.1 Hz, 1H), 5.04 (t, *J* = 6.7 Hz, 1H), 2.24-2.18 (m, 2H), 2.15-2.10 (m, 2H), 2.02 (q, *J* = 7.6 Hz, 2H), 1.85 (d, J = 1.0 Hz, 3H), 1.69 (d, *J* = 1.1 Hz, 3H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 147.9, 138.1, 122.7, 74.7, 39.8, 26.0, 24.8, 24.0, 22.9, 12.8; MS (EI) 137 (100, M^+-I), 95 (22), 83 (42), 55 (100).

Procedure for the synthesis of 2-(chloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 22.



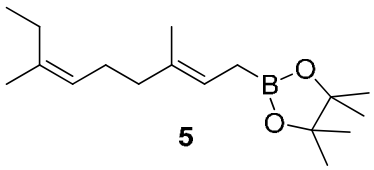
22

Prepared according to a procedure modified from Whiting.[xii]

A stirred solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.5 ml, 41.6 mmol) and chloroiodomethane (3.3 ml, 45.8 mmol) in anhydrous THF (40 ml) was cooled to – 78 °C. *n*BuLi (28.6 mL, 45.8 mmol, 1.6M in hexanes) was then added dropwise and after stirring for 30 min at this temperature chlorotrimethylsilane (6.4 ml, 49.9 mmol) was added (again dropwise). After 10 min the flask was removed from the cooling bath and the contents were allowed to stir at RT for 24 h. H_2O (50 ml) was added and the mixture extracted with Et_2O (2 × 100 ml). The organics were combined, washed (H_2O, 2 × 50 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (gradient elution, SiO_2 5% EtOAc / petrol to 10% EtOAc / petrol, R_f = 0.3 [10% EtOAc / petrol]). Column length ~10 cm to reduce material loss). The boronate was then further purified by distillation (68 - 70 °C, 20 Torr) to yield a colourless oil (5.8 g, 80%). The compound was contaminated with 7% of the corresponding iodomethyl boronate and was used without further purification. Spectra were in accordance with the published data.[xiii]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.94 (s, 2H), 1.27 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) 84.6, 24.7; ^{11}B NMR ($CDCl_3$, 128 MHz) 31.4. MS (EI) 176 (M^+, 5), 161 (100), 134 (5), 118 (7), 85 (35), 77 (7), 59 (25).

Procedure for the synthesis of (2*E*, 6*Z*) 3,7-dimethyl-2,6-nonadiene-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 5.



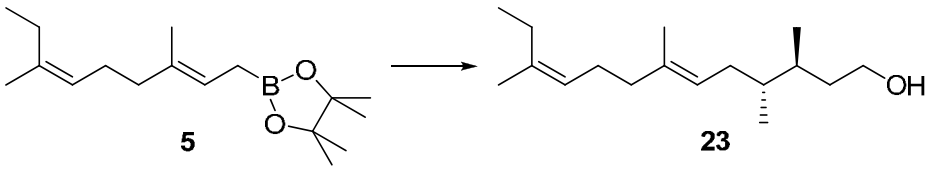
5

Prepared according to a procedure modified from Hoffmann *et al*.[xiv]

To a solution of iodide **21** (553 mg, 2.1 mmol) in dry Et_2O (25 ml) and dry hexane (15 ml) at – 78 °C under argon was added *t*BuLi (2.6 mL, 4.2 mmol, 1.6M in pentane) dropwise. After 30 min at this temperature chloromethylboronate **22** (370 mg, 2.1 mmol) was added. After 10 min at – 78 °C the reaction mixture was removed from the cooling bath and stirred for a further 2 h at RT. The reaction mixture was then cooled to 0 °C and H_2O (10 ml) was added. The mixture was extracted with Et_2O (2 × 50 ml). The organics were washed with H_2O (2 × 30 ml), dried ($MgSO_4$) and concentrated *in vacuo* to give a pale yellow oil. The crude product was purified by flash chromatography (SiO_2, 5% Et_2O / petrol, R_f = 0.5, ~8 cm to reduce material loss) to yield the boronate as a clear oil (312 mg, 1.1 mmol, 53%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.25 (tq, *J* = 7.8, 1.5 Hz, 1H), 5.08 (t, *J* = 6.4 Hz, 1H), 2.08-1.99 (m, 6H), 1.67 (q, *J* = 1.2 Hz, 3H), 1.63-1.61 (m, 2H), 1.59 (d, *J* = 1.5 Hz, 3H), 1.25 (s, 12H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 136.9, 135.1, 124.1, 118.5, 83.0, 40.0, 26.4, 24.8, 24.7, 22.8, 15.9, 12.8; ^{11}B NMR ($CDCl_3$, 96 MHz) 32.2; Anal. Calcd for $C_{17}H_{31}BO_2$: C, 73.38; H, 11.23. Found: C, 73.57; H, 11.29; MS (EI) 278 (M^+), 263 (M^+-CH_3), 249 (M^+-Et), 195, 95, 83.

Procedure for the synthesis of 3*S*,4*R*-(6*E*,10*Z*)-3,4,7,11-tetramethyl-6,10-tridecadien-1-ol 23 (With $MgBr_2$).



5 **23**

To a solution of ethyl carbamate **3** (260 mg, 1.5 mmol) and (-)-sparteine (340 µL, 1.5 mmol) in dry Et_2O (7.5 mL) at –78 °C under argon was added *s*BuLi (1.15 mL, 1.5 mmol, 1.3 M in cyclohexane) dropwise. This mixture was then stirred at –78 °C for 5h before addition of **5** (278 mg, 1.0 mmol) in Et_2O (2 mL) dropwise. The reaction was stirred for a further hour at –78 °C before addition of a freshly made solution of $MgBr_2$ (from stirring Mg turnings (60 mg, 2.5 mmol) and 1,2-dibromoethane (130 µL, 1.57 mmol) in Et_2O (3. mL) at room temperature for 4 h). The reaction was stirred for a further 30 min at –78 °C, warmed to room temperature, heated to reflux and then stirred for ≥ 12 h.

The reaction mixture was cooled to room temperature and the crude boronic ester **4** just obtained was then added at – 78 °C to a second solution of freshly made lithiated carbamate **3** (1.5 mmol, as above). After stirring for 1.5 h at -78 °C, a freshly made solution of $MgBr_2$ was added (1.5 mmol, as above) and the reaction mixture heated to reflux for ≥ 12 h.

The crude mixture of **2** was cooled to room temperature and then to -78 °C before addition of a freshly made vinyllithium solution (1.8 mL, 5.0 mmol, ~ 2.8 M, see below).

Preparation of vinyllithium solution[iv]: ^{n}BuLi (2.5 M in hexanes, 3.8 mL, 6.0 mmol) was added dropwise at room temperature to tetravinyltin (550 µL, 3.0 mmol) in a flame dried Schlenk tube under argon. After stirring for 30 minutes, the liquid was removed by cannula and the white solid was washed with dry pentane (4 x 2 mL). The remaining solid was diluted in THF (1.8 mL) and the solution was titrated (~ 2.8 M).

After stirring the mixture for an additional 45 minutes at -78 °C, a solution of I_2 (1.27 g, 5.0 mmol) in MeOH (28 mL) was added, followed 30 minutes later by a solution of MeONa (580 mg, 10.0 mmol) in MeOH (10 mL). The mixture was then allowed to stir at room temperature for 1 h and concentrated. The crude was taken up into Et_2O

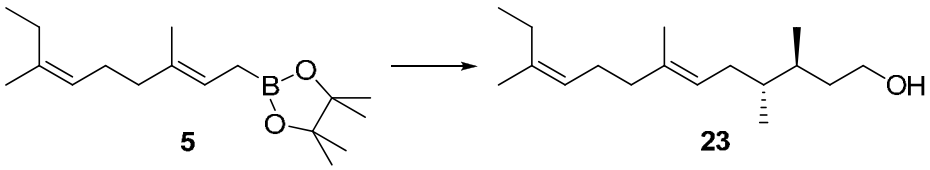
(130 mL) and washed successively with 5% NaS_2O_3 solution, 5% NaOH solution, 5% NaOH solution containing 10% H_2O_2, 5% NaS_2O_3 solution again and finally brine. The ethereal layer was then dried ($MgSO_4$) and concentrated *in vacuo*.

To the crude triene in Et_2O (8 mL) at 0 °C under argon was added a 0.5 M solution of 9-BBN (made from 366 mg of dimer, 1.5 mmol, in 6.0 mL of THF). The cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 2.5 h. The mixture was then cooled to 0 °C and a pre-mixed solution of NaOH (2 M) / H_2O_2 (30%) (2:1 v/v, 12.0 mL) was added. After 30 minutes, the mixture was poured onto $NaHCO_3$ sat. solution (50 mL) and extracted with Et_2O (75 mL). The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 20% Et_2O in petrol, R_f = 0.3) to yield **23** as a yellow oil (173 mg, 69%).

All spectral data were in accordance with literature values.[xv]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.12 (t, *J* = 7.8 Hz, 1H), 5.06 (t, *J* = 7.0 Hz, 1H), 3.76-3.70 (m, 1H), 3.66-3.60 (m, 1H), 2.11-1.97 (m, 8H), 1.85-1.77 (m, 1H), 1.71-1.30 (m, 3H), 1.68 (d, *J* = 1.1 Hz, 3H), 1.60 (s, 3H), 1.28-1.20 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 137.0, 135.3, 124.0, 123.9, 61.7, 40.2, 38.7, 35.9, 33.6, 31.5, 26.2, 24.8, 22.8, 16.7, 16.1, 16.0, 12.8; MS (EI) 252 (M^+), 195 (M^+-EtMeC=), 137, 123, 109, 95, 83, 69, 55; $[\alpha]^{23}_D$ = - 2.6 (*c* 2.64, $CHCl_3$) (d.r. = 94:6, see spectra below), Lit.[xv]: $[\alpha]^{22}_D$ = - 4.5 (*c* 4.87, $CHCl_3$) (d.r. = 94:6).

Procedure for the synthesis of 3*S*,4*R*-(6*E*,10*Z*)-3,4,7,11-tetramethyl-6,10-tridecadien-1-ol 23 (Without $MgBr_2$).



5 **23**

To a solution of ethyl carbamate **3** (260 mg, 1.5 mmol) and (-)-sparteine (340 µL, 1.5 mmol) in dry Et_2O (7.5 mL) at –78 °C under argon was added *s*BuLi (1.15 mL, 1.5 mmol, 1.3 M in cyclohexane) dropwise. This mixture was then stirred at –78 °C for 5h before addition of **5** (278 mg, 1.0 mmol) in Et_2O (2 mL) dropwise. The reaction was stirred for a further 30 min at –78 °C, warmed to room temperature, heated to reflux and then stirred for ≥ 12h.

The reaction mixture was cooled to room temperature and the crude boronic ester **4** just obtained was then added at – 78 °C to a second solution of freshly made lithiated carbamate **3** (1.5 mmol, as above). After stirring for 30 min at -78 °C the reaction mixture heated to reflux for ≥ 12h.

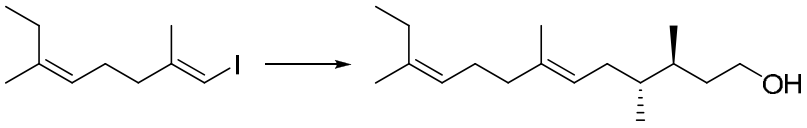
The crude mixture of **2** was cooled to room temperature and then to -78 °C before addition of a freshly made vinyllithium solution (1.8 mL, 5.0 mmol, ~ 2.8 M, as above).

After stirring the mixture for an additional 45 minutes at -78 °C, a solution of I_2 (1.27 g, 5.0 mmol) in MeOH (28 mL) was added, followed 30 minutes later by a solution of MeONa (580 mg, 10.0 mmol) in MeOH (10 mL). The mixture was then allowed to stir at room temperature for 1 h and concentrated. The crude was taken up into Et_2O (130 mL) and washed successively with 5% NaS_2O_3 solution, 5% NaOH solution, 5% NaOH solution containing 10% H_2O_2, 5% NaS_2O_3 solution again and finally brine. The ethereal layer was then dried ($MgSO_4$) and concentrated *in vacuo*.

To the crude triene in Et_2O (8 mL) at 0 °C under argon was added a 0.5 M solution of 9-BBN (made from 366 mg of dimer, 1.5 mmol, in 6.0 mL of THF). The cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 2.5 h. The mixture was then cooled to 0 °C and a pre-mixed solution of NaOH (2 M) / H_2O_2 (30%) (2:1 v/v, 12.0 mL) was added. After 30 minutes, the mixture was poured onto $NaHCO_3$ sat. solution (50 mL) and extracted with Et_2O (75 mL). The aqueous layer was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*.

The crude product was purified by flash chromatography (SiO_2, 20% Et_2O in petrol, R_f = 0.3) to yield **23** as a yellow oil (143 mg, 57%).
Data as above.

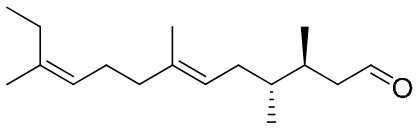
Procedure for the synthesis of 3*S*,4*R*-(6*E*,10*Z*)-3,4,7,11-tetramethyl-6,10-tridecadien-1-ol 23 (from vinyl iodide 21).



21 **23**

To a solution of iodide **21** (264 mg, 1.0 mmol) in dry Et_2O (12.5 ml) and dry hexane (7.5 ml) at – 78 °C under argon was added *t*BuLi (1.25 mL, 2.0 mmol, 1.6M in pentane) dropwise. After 30 min at this temperature chloromethylboronate **22** (176 mg, 1.0 mmol) was added. After 10 min at – 78 °C the reaction mixture was removed from the cooling bath and stirred for a further 2 h at RT. The reaction mixture was then cooled to 0 °C and H_2O (10 ml) was added. The mixture was extracted with Et_2O (2 × 50 ml). The organics were washed with H_2O (2 × 30 ml), dried ($MgSO_4$) and concentrated to give a pale yellow oil. The crude product in Et_2O (2 ml) was then added onto a solution of freshly made lithiated carbamate **3** (1.5 mmol) and the remaining of the procedure carried out as above (without $MgBr_2$).
The crude product was purified by flash chromatography (SiO_2, 20% Et_2O in petrol, R_f = 0.3) to yield **23** as a colourless oil (100 mg, 40%).
Data as above.

Procedure for the synthesis of (+)-3*S*,4*R*-(6*E*,10*Z*)-3,4,7,11-tetramethyl-6,10-tridecadienal 1 ((+)-faranal).[xv]



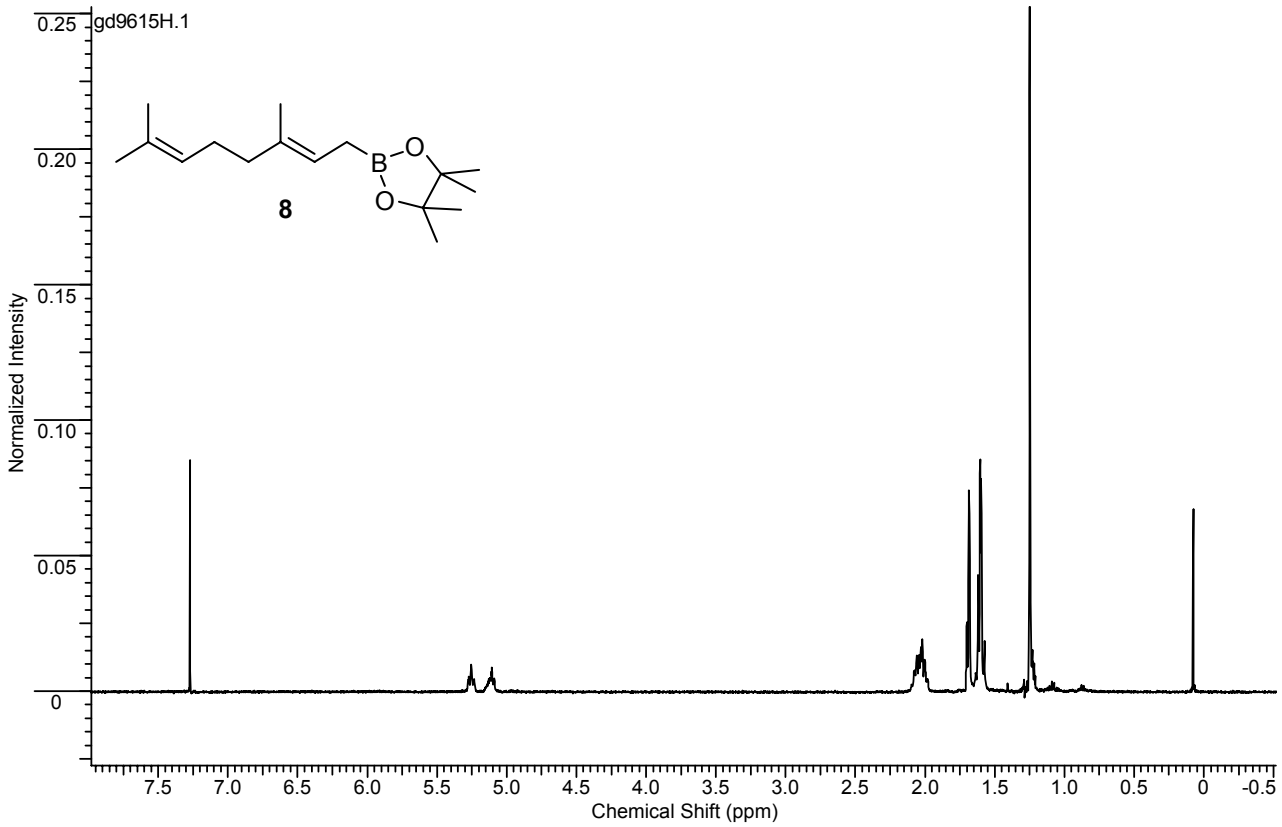
1

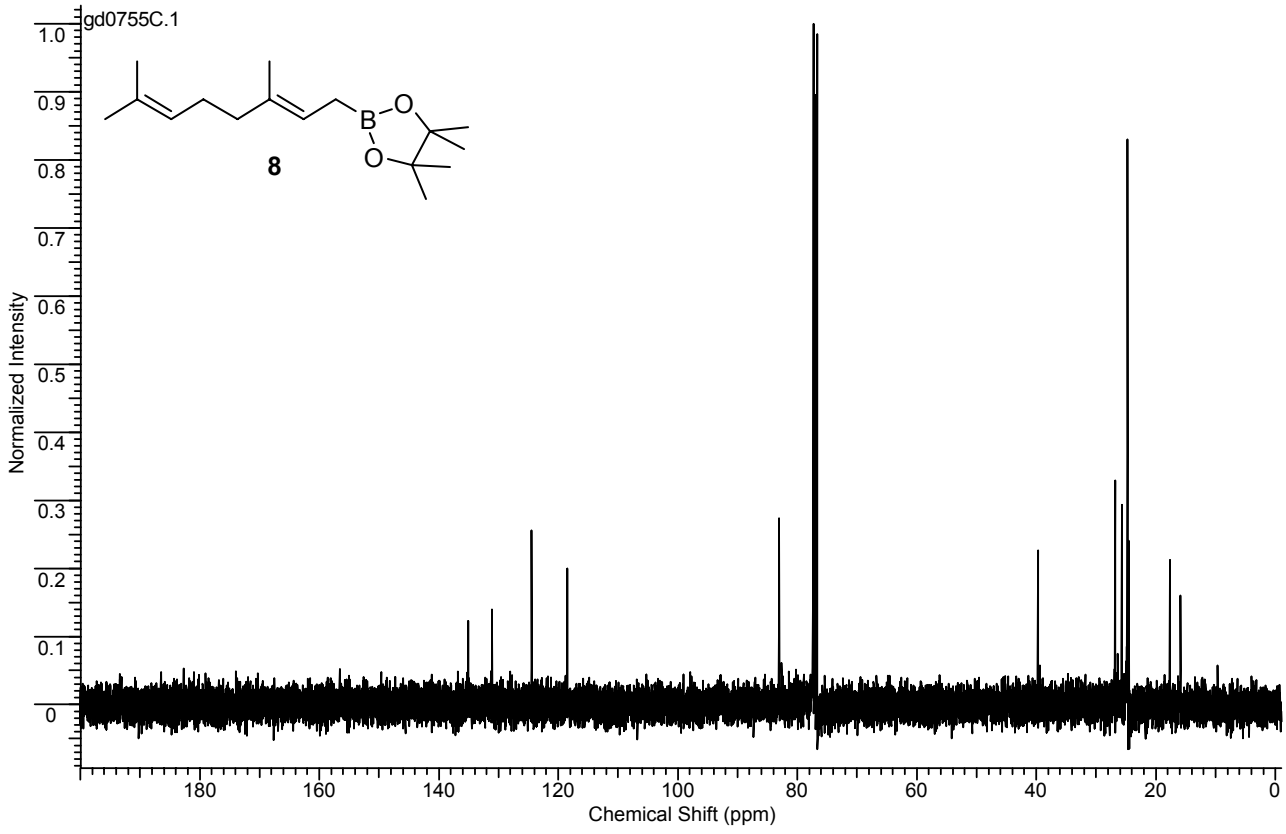
To a solution of alcohol **23** (70 mg, 0.28 mmol) in dry DCM (4 mL) at room temperature was added PDC (210 mg, 0.55 mmol) portionwise. This mixture was then stirred for 3h and then filtered on a short silica pad. The solids were washed with Et_2O (20 mL) and the organic solution carefully concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 10% Et_2O/petrol) to yield **1** as a colourless oil (53 mg, 76%).

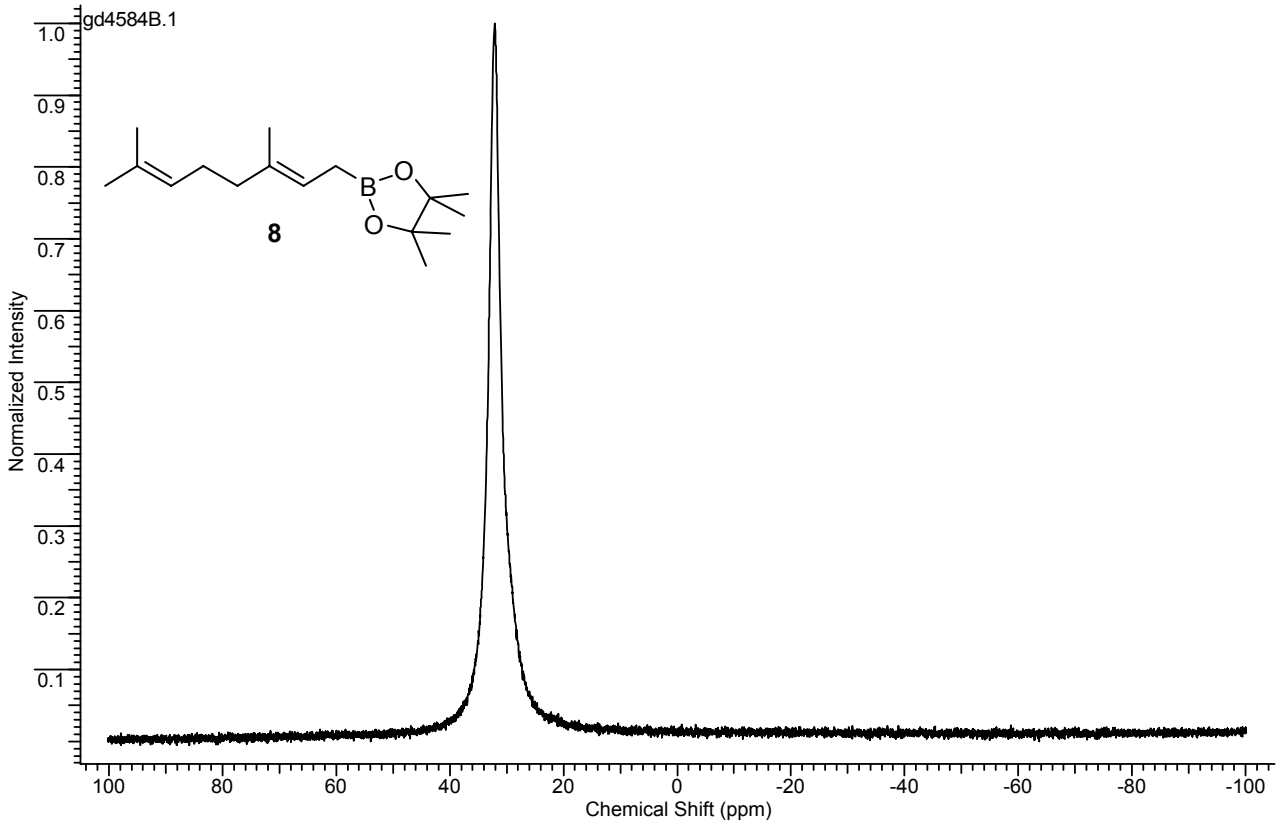
All spectral data were in accordance with literature values.[xv]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.75 (dd, *J* = 3.1, 1.7 Hz, 1H), 5.11 (tq, *J* = 7.1, 1.2 Hz, 1H), 5.05 (t, *J* = 7.1 Hz, 1H), 2.44 (ddd, *J* = 15.4, 3.4, 1.7 Hz, 1H), 2.18 (ddd, *J* = 15.4, 6.5, 3.1 Hz, 1H), 2.13-1.96 (m, 8H), 1.87-1.78 (m, 1H), 1.67 (d, *J* = 1.1 Hz, 3H), 1.60 (s, 3H), 1.51-1.44 (m, 1H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 203.0, 137.1, 135.9, 124.2, 123.5, 47.4, 40.1, 38.5, 32.1, 31.8, 26.2, 24.4, 23.0, 17.8, 17.3, 16.2, 12.6; MS (EI) 250 (M^+), 232, 203, 193, 175, 137, 123, 107, 95, 83, 55; $[\alpha]^{23}_D$ = + 16.7 (*c* 1.56, $CHCl_3$), Lit.[xv]: $[\alpha]^{23}_D$ = + 17.4 (*c* 4.12, $CHCl_3$).

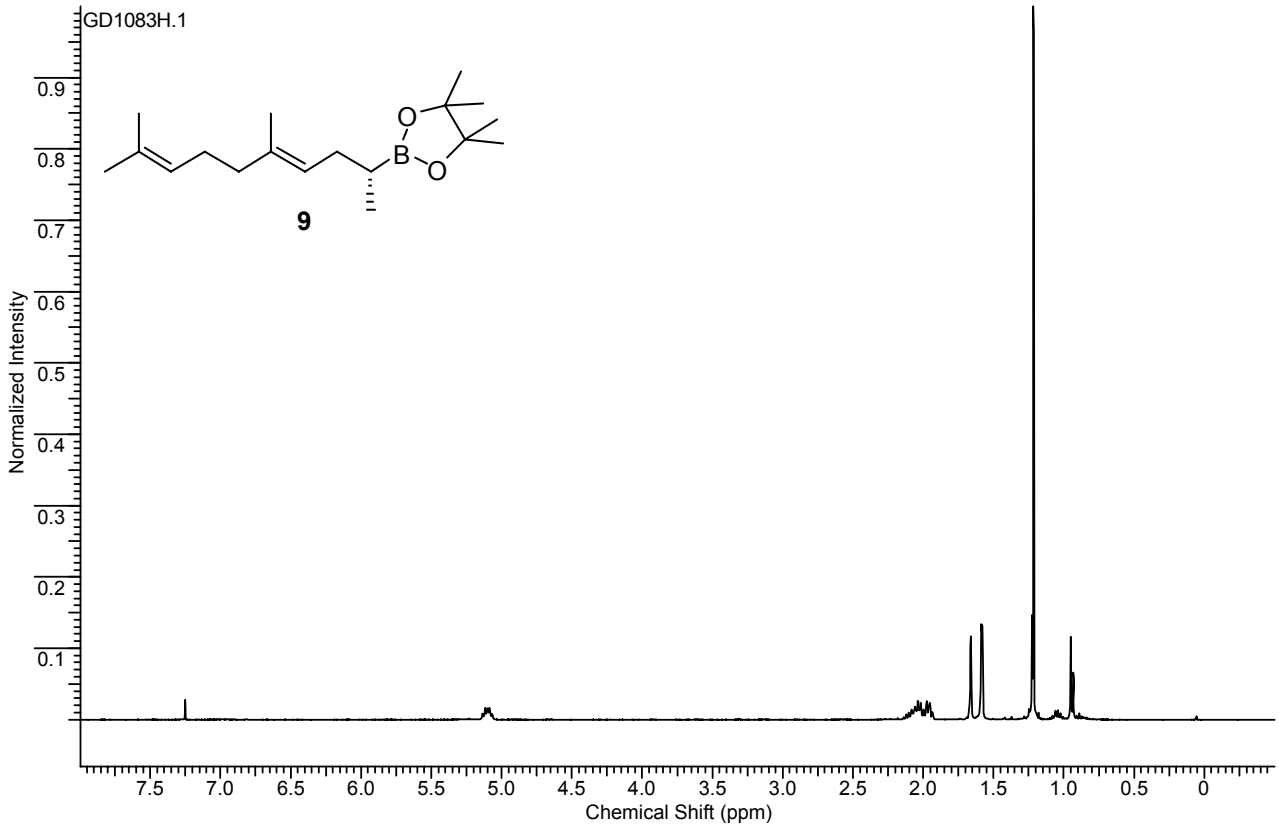
3. ^{1}H, ^{13}C and ^{11}B spectra:



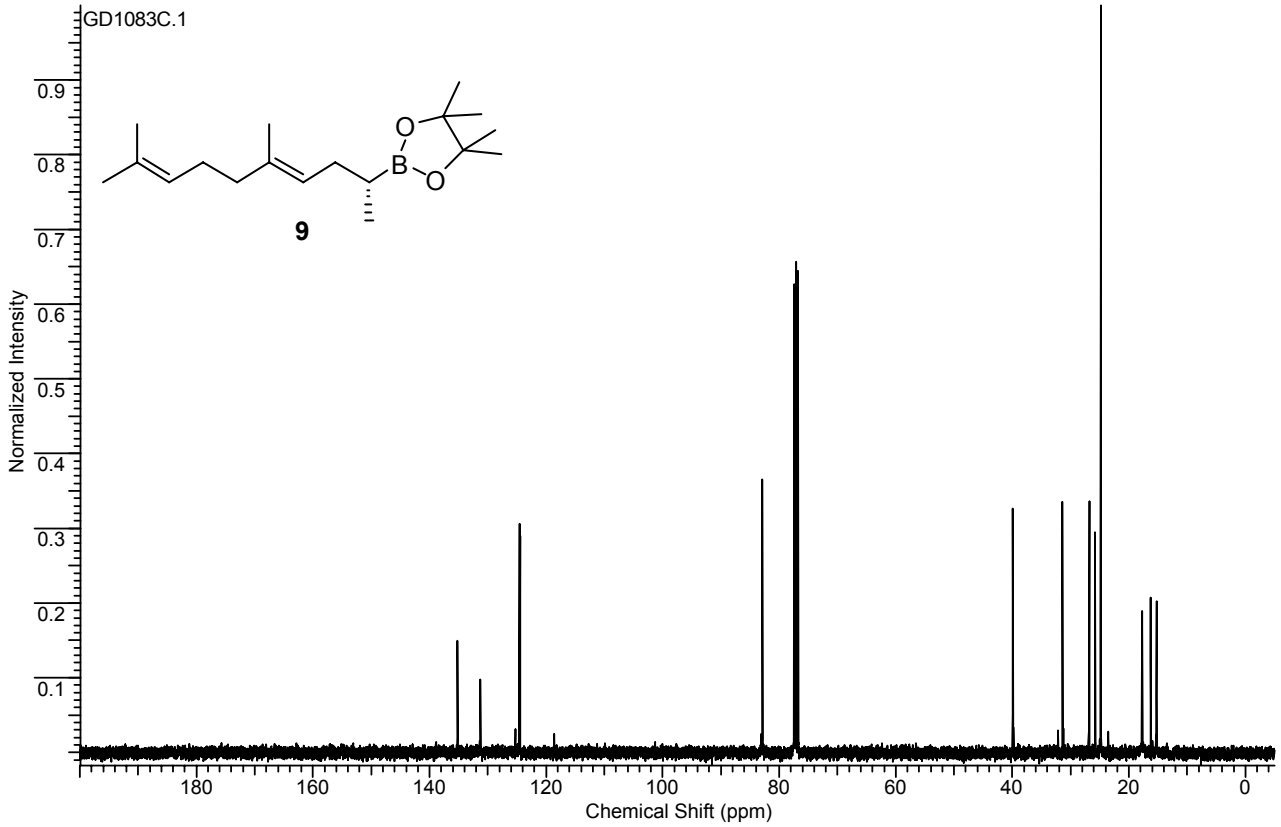


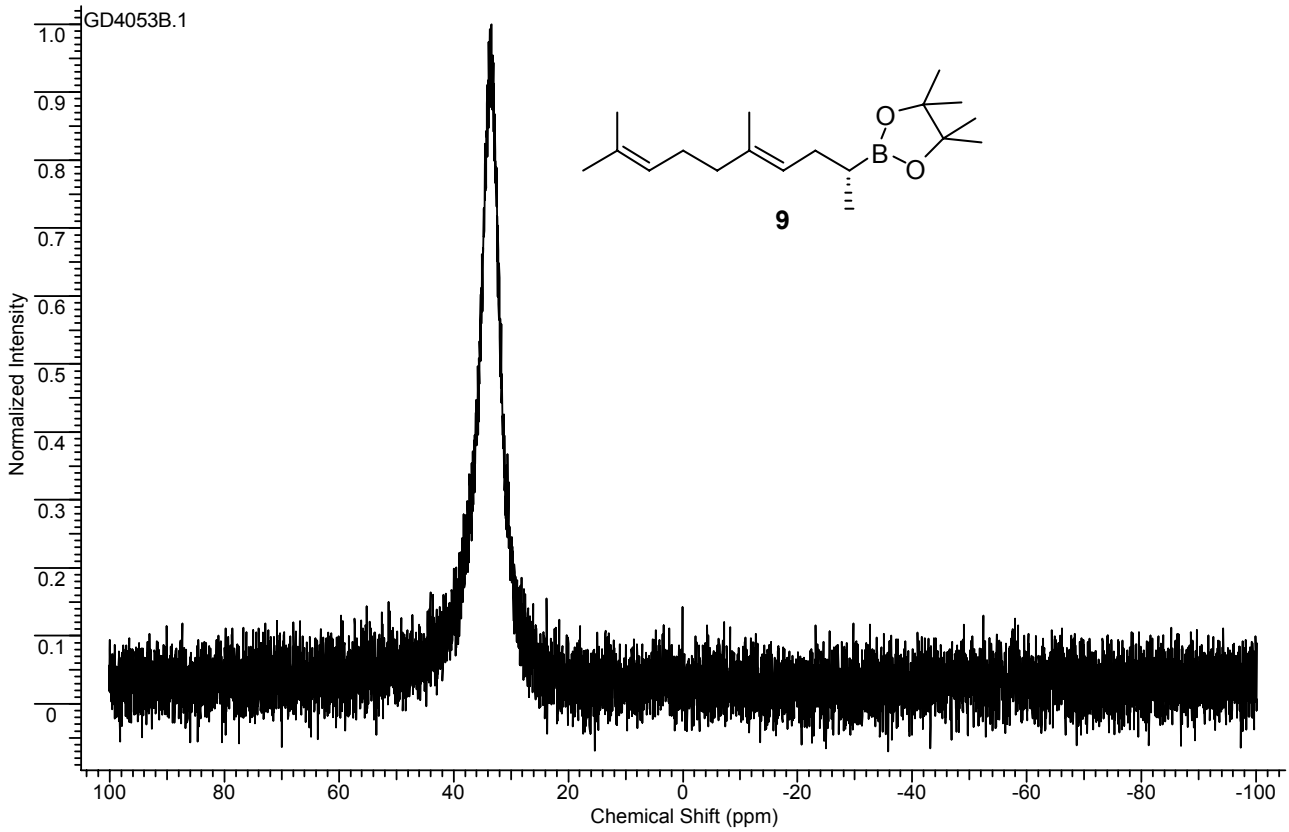

gd4584B.1
Normalized Intensity
Chemical Shift (ppm)
B
O
O

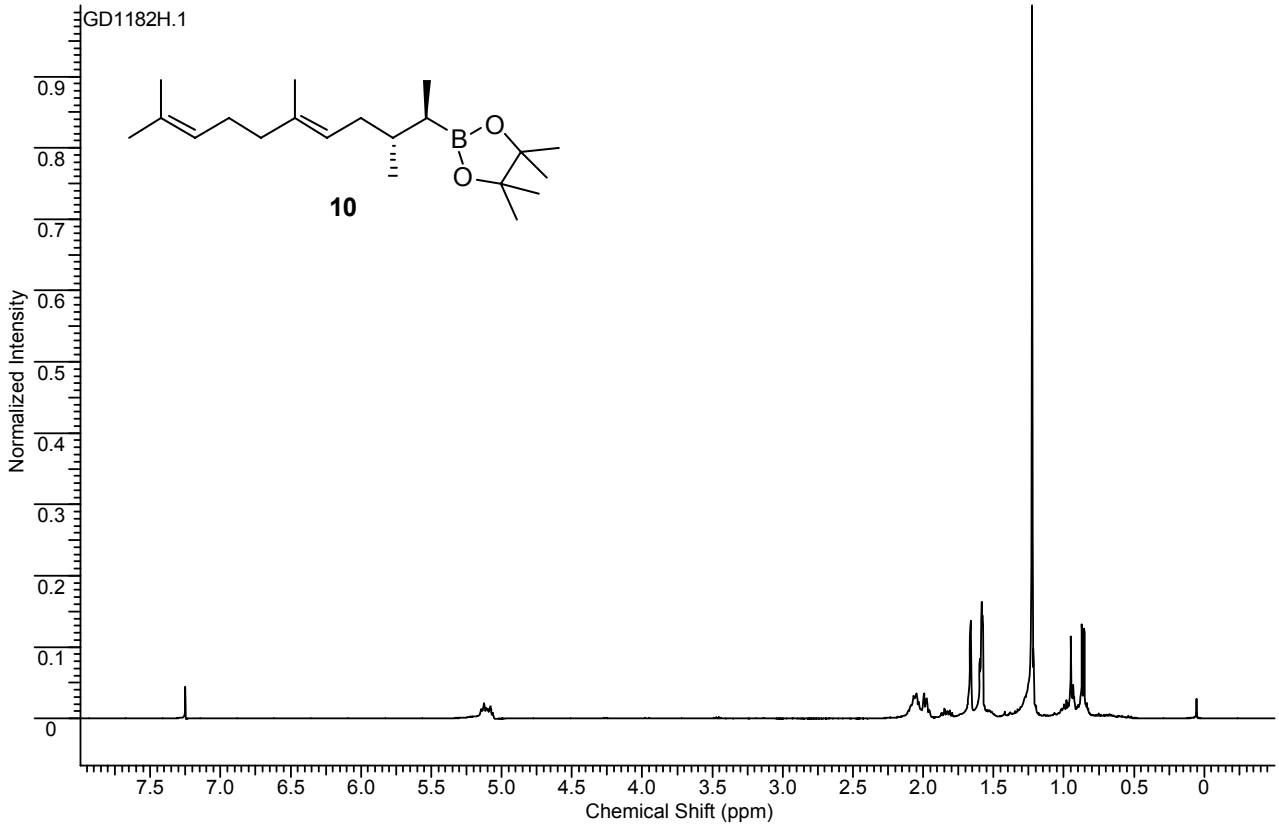
8

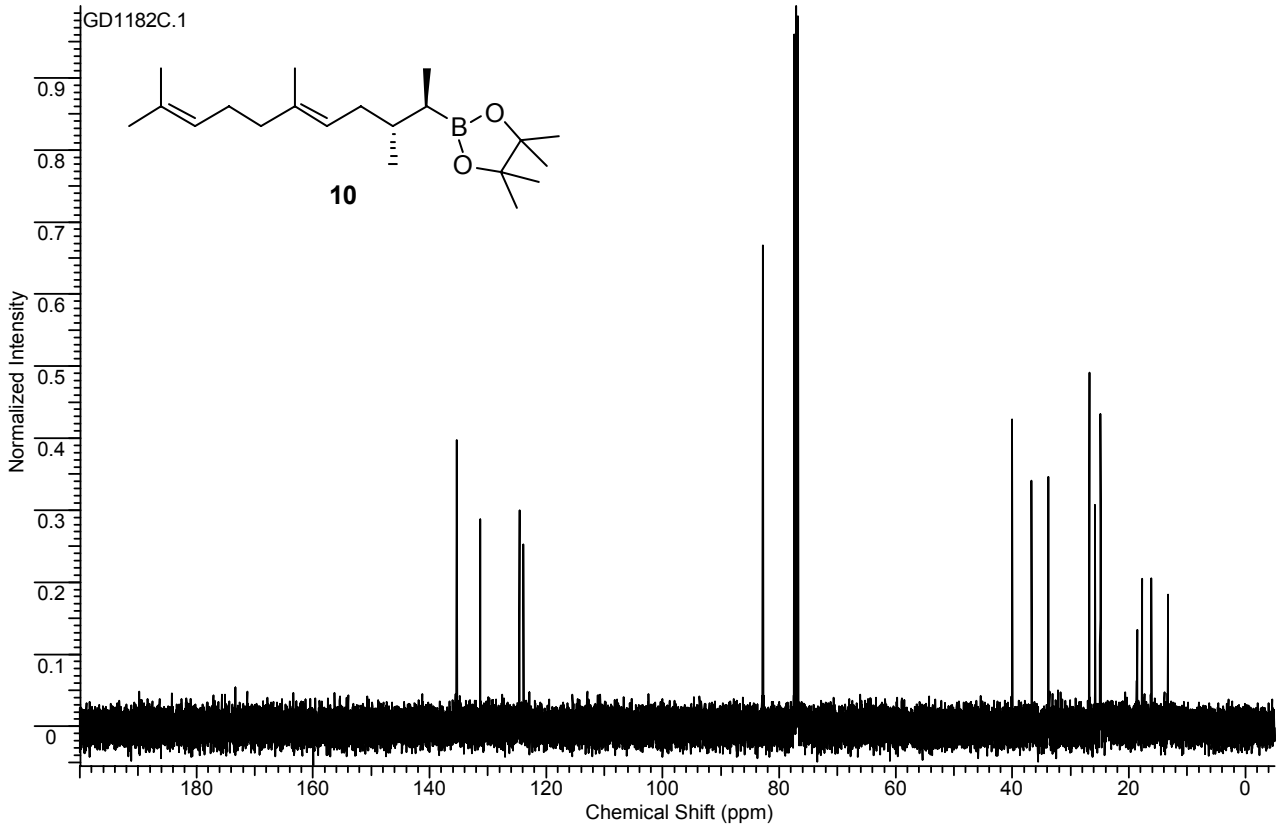

GD1083H.1
Normalized Intensity
Chemical Shift (ppm)
B
O
O

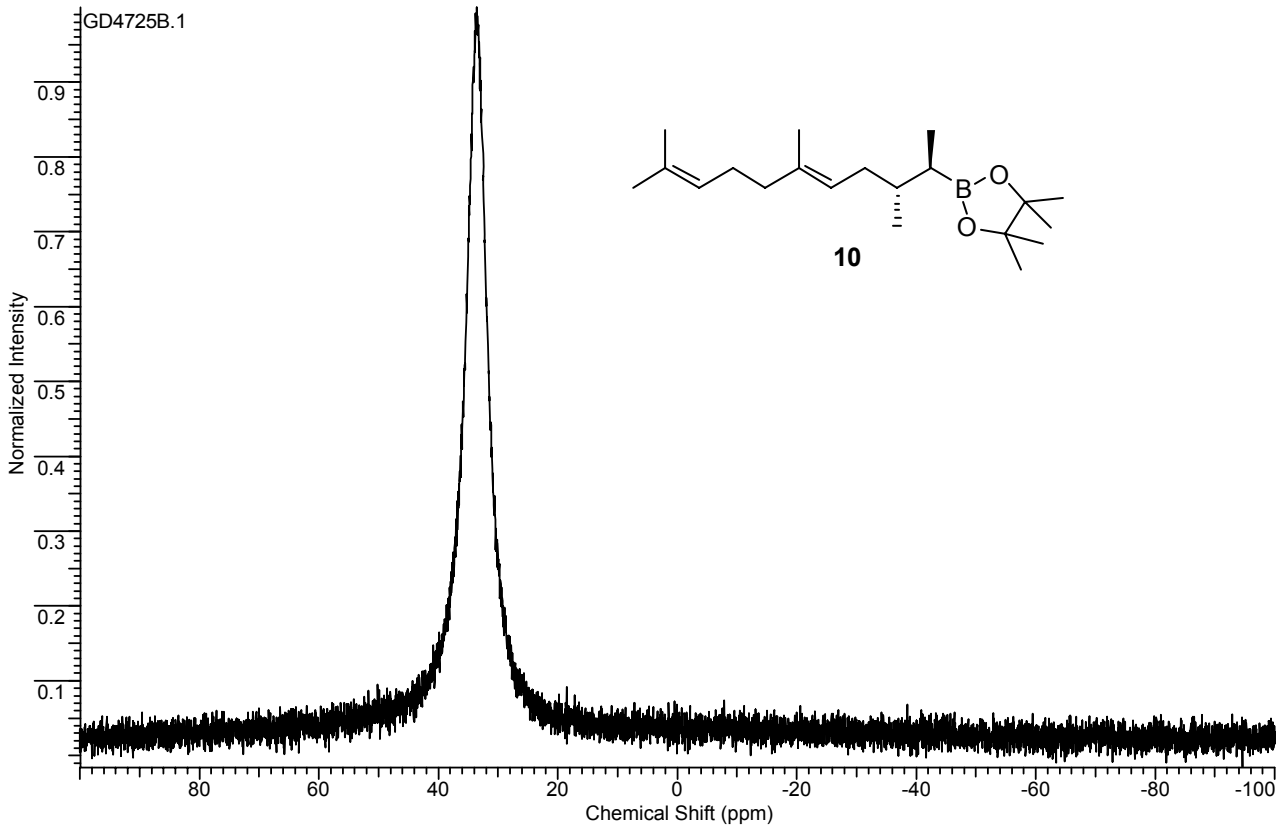
9


GD1083C.1
O
B
O
9
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

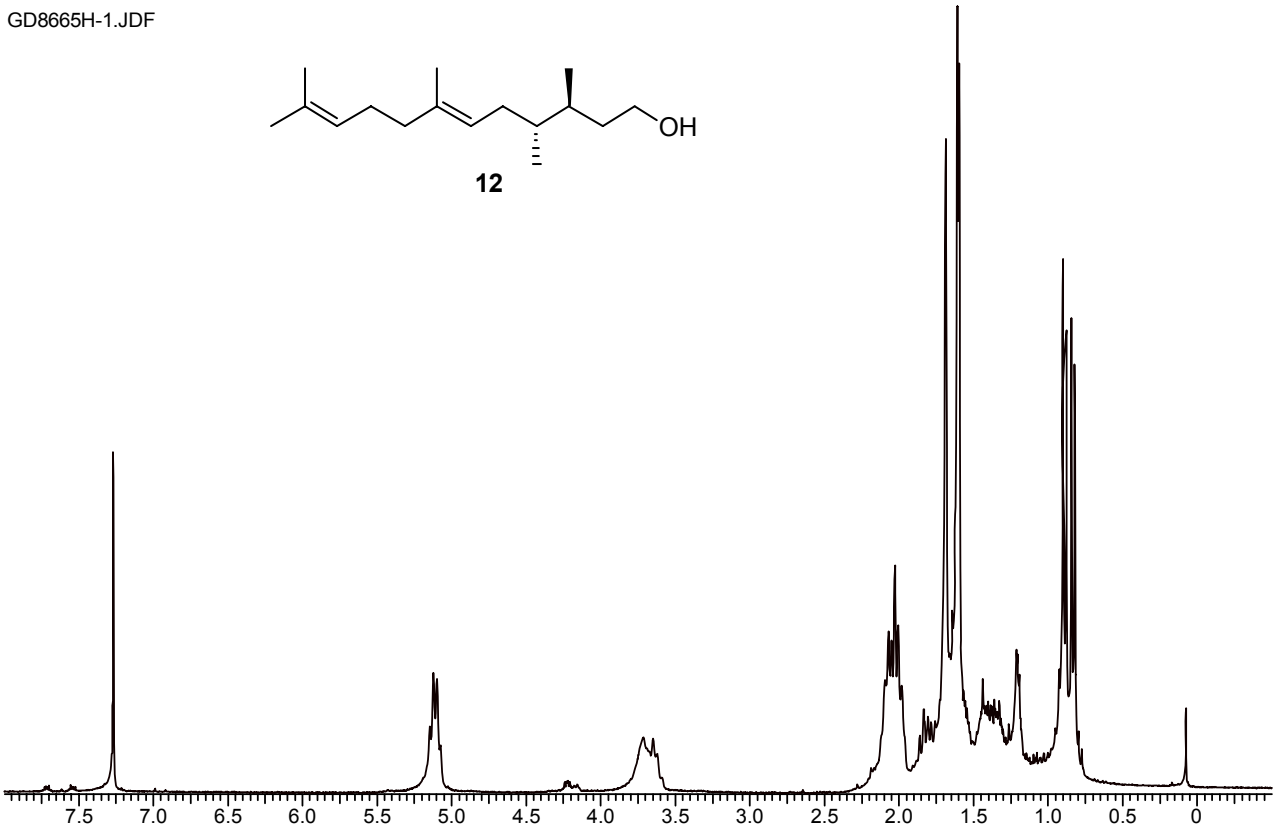

GD4053B.1
O
B
O
9
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
80
60
40
20
0
-20
-40
-60
-80
-100
Chemical Shift (ppm)


GD1182H.1
10
Normalized Intensity
Chemical Shift (ppm)

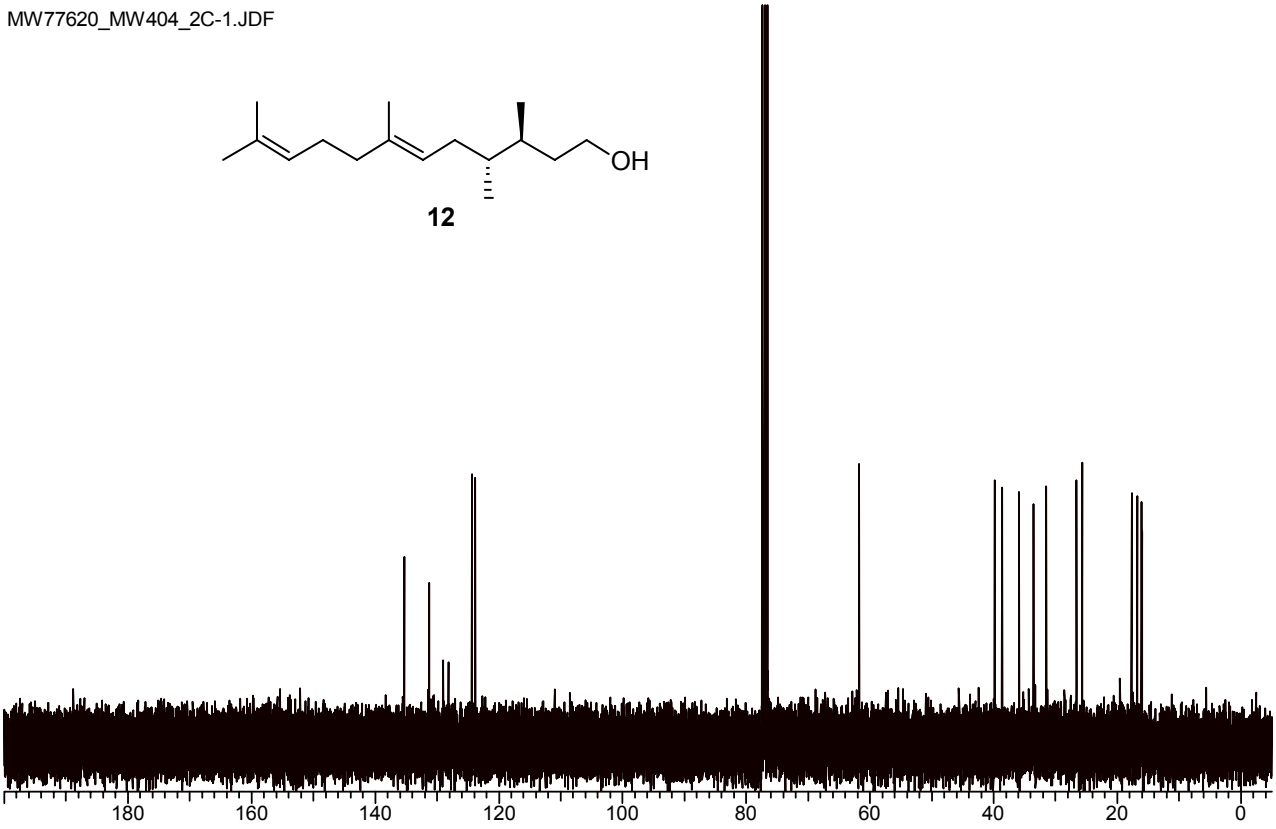

GD1182C.1
10
Normalized Intensity
Chemical Shift (ppm)


GD4725B.1
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
80
60
40
20
0
-20
-40
-60
-80
-100
Chemical Shift (ppm)
B
O
O

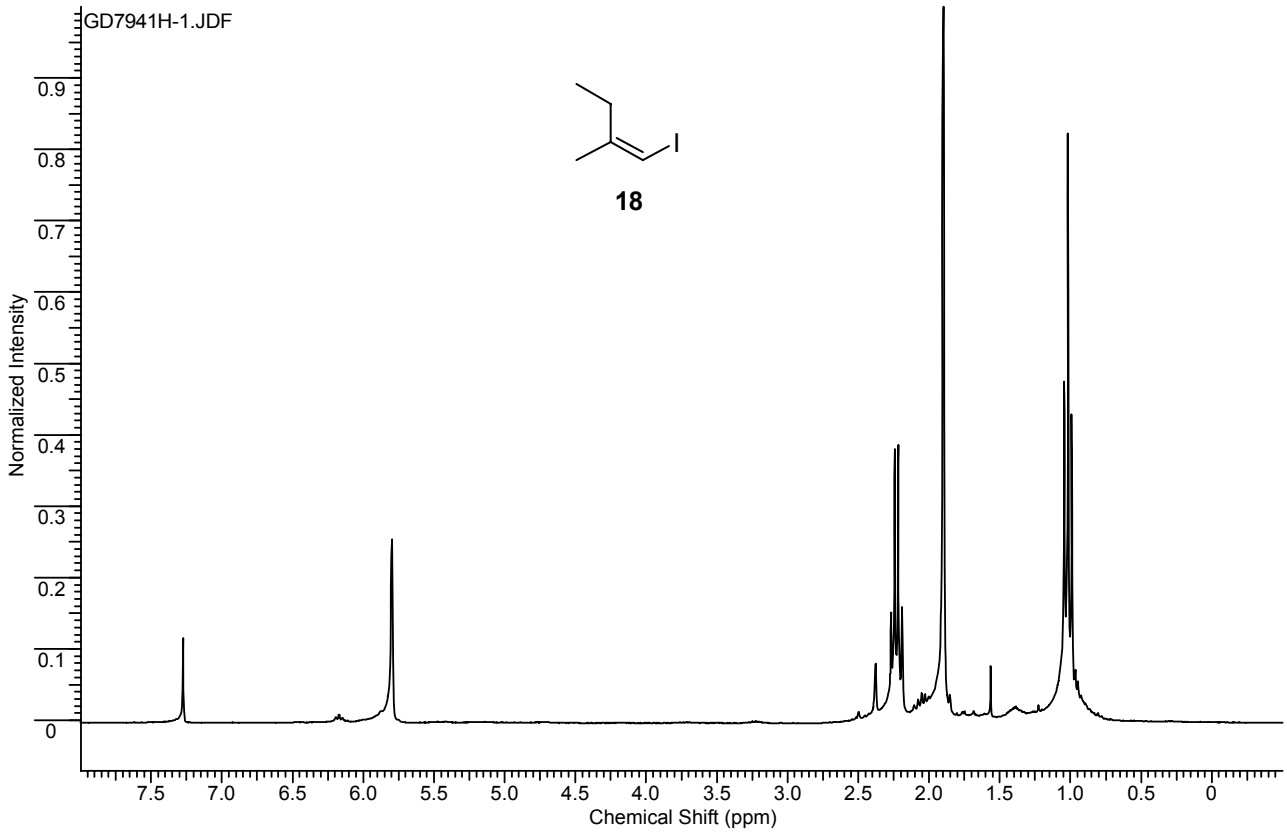
10


GD8665H-1.JDF
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

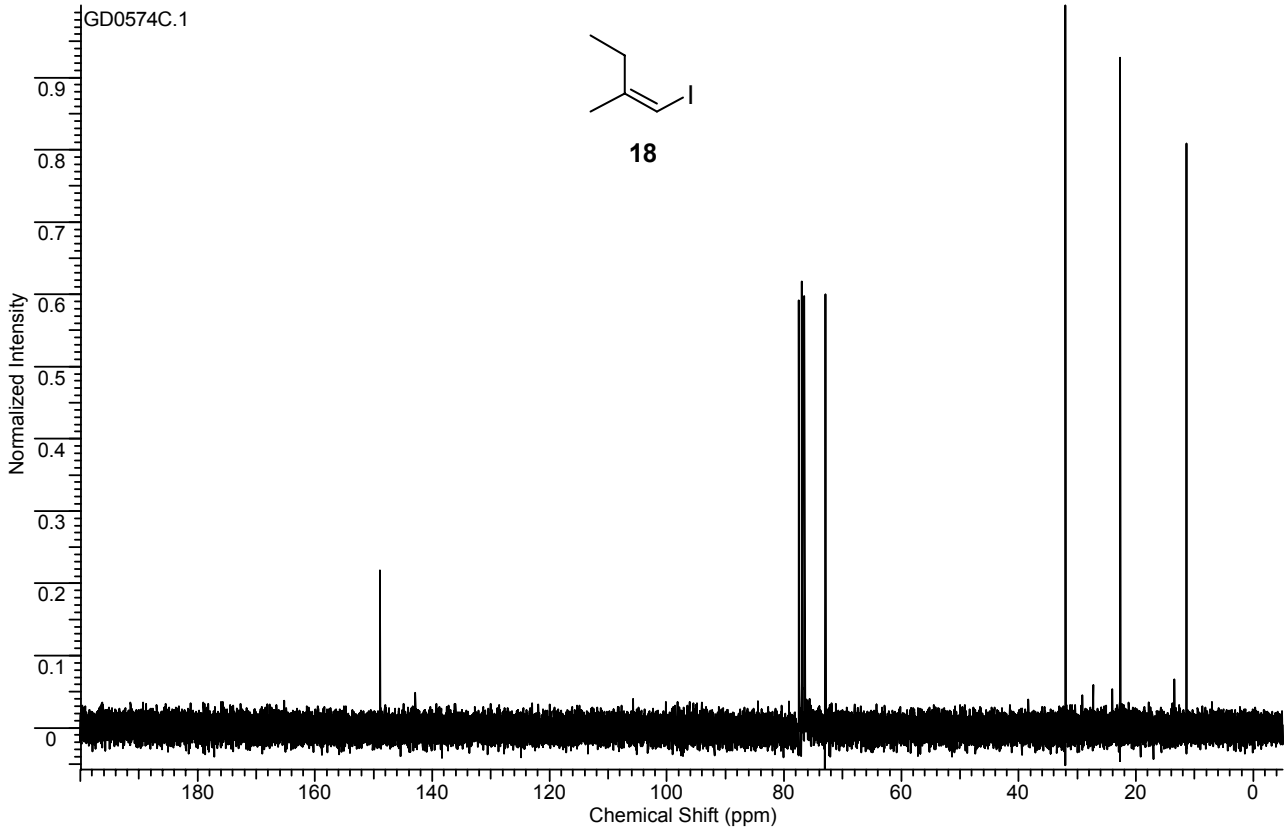
12

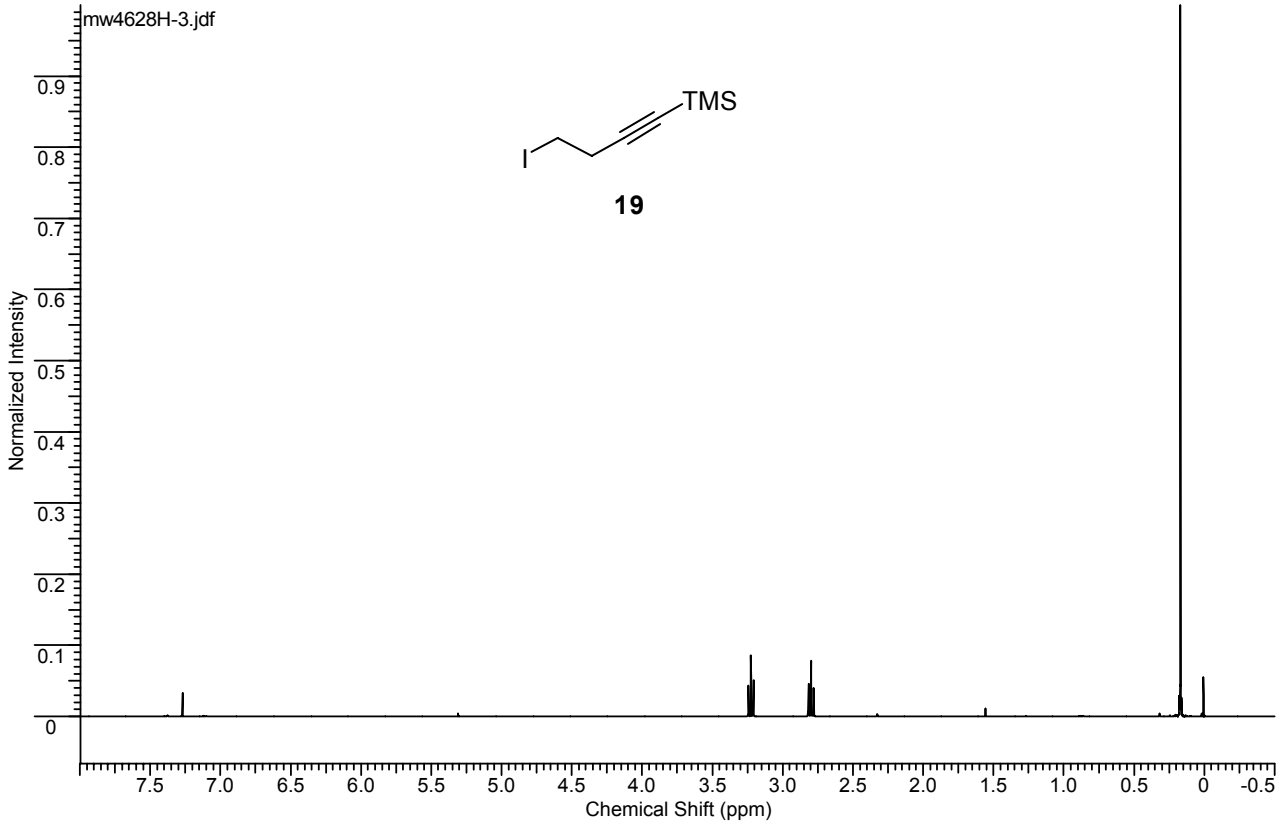

MW77620_MW404_2C-1.JDF
OH
180
160
140
120
100
80
60
40
20
0

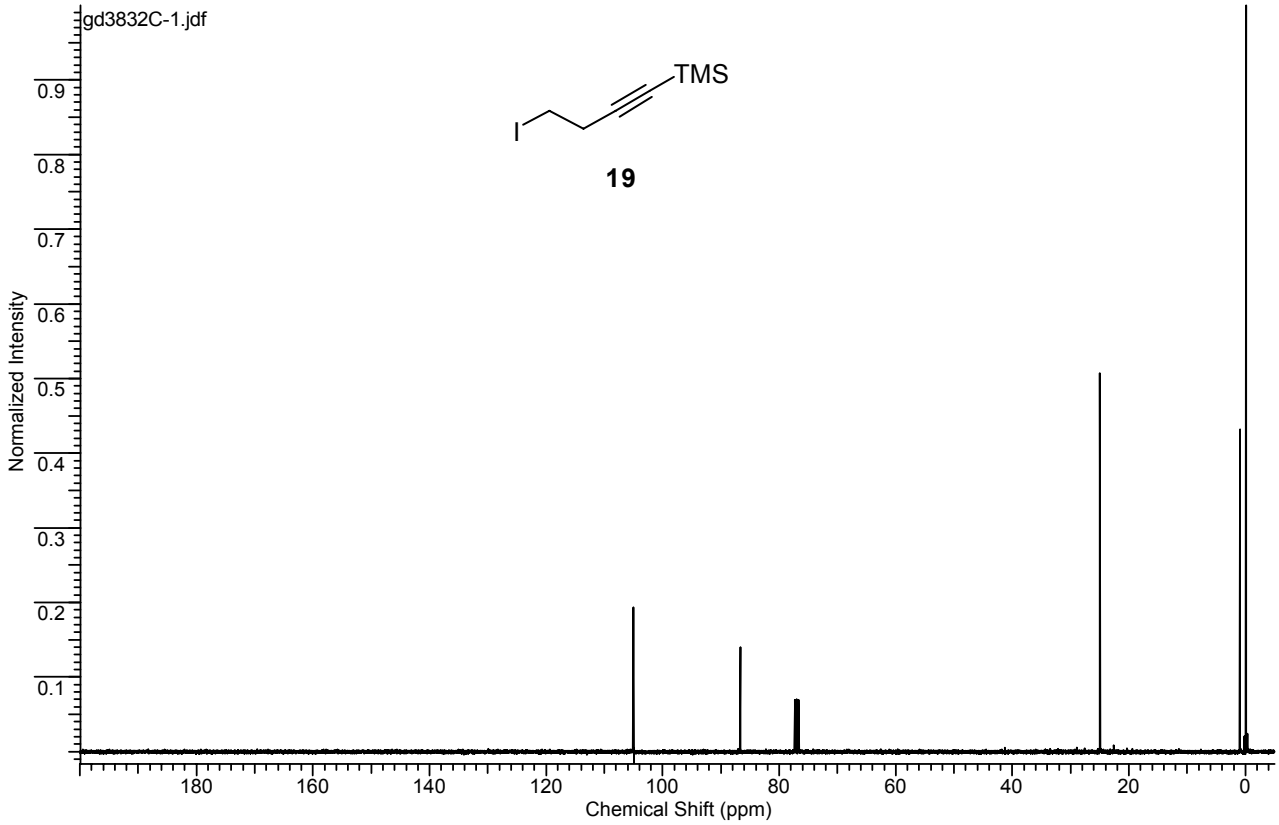
12

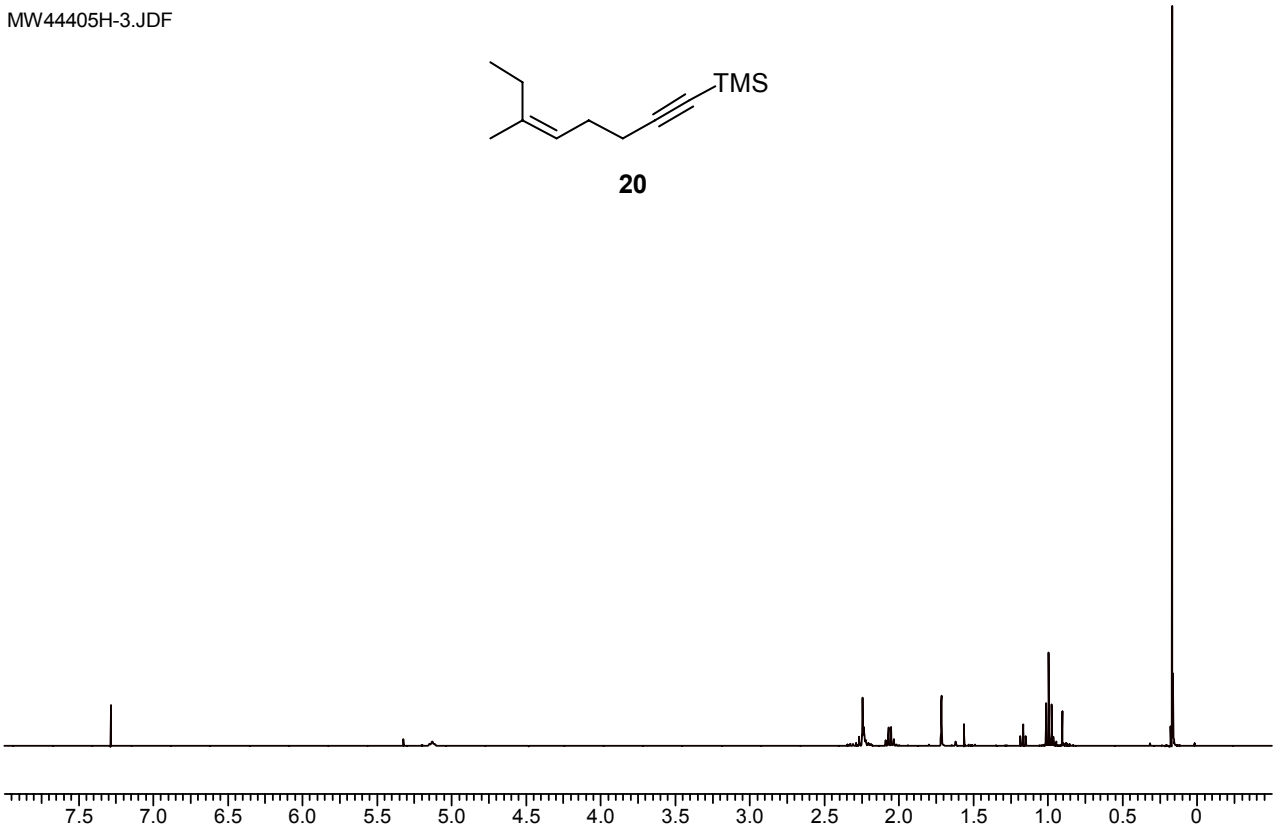

GD7941H-1.JDF
I
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

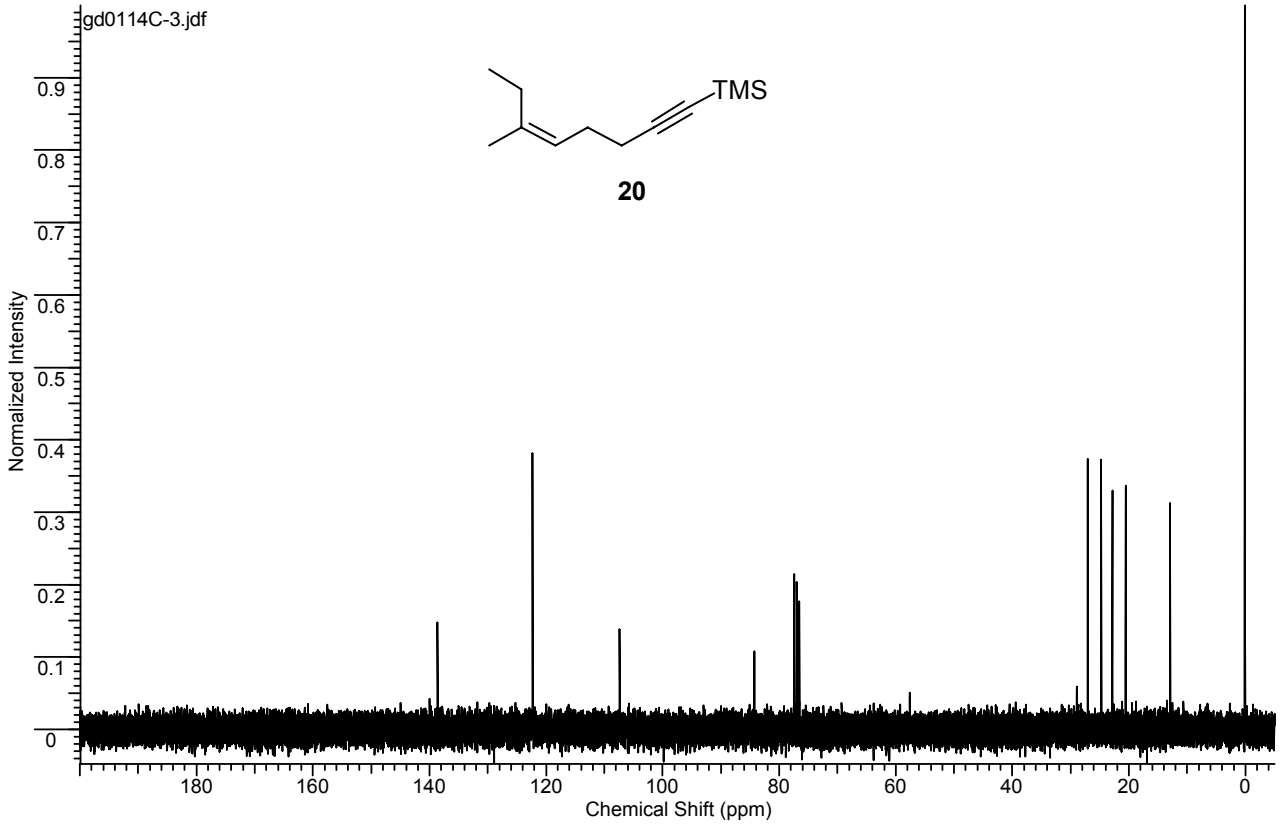
18


GD0574C.1
I
18
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

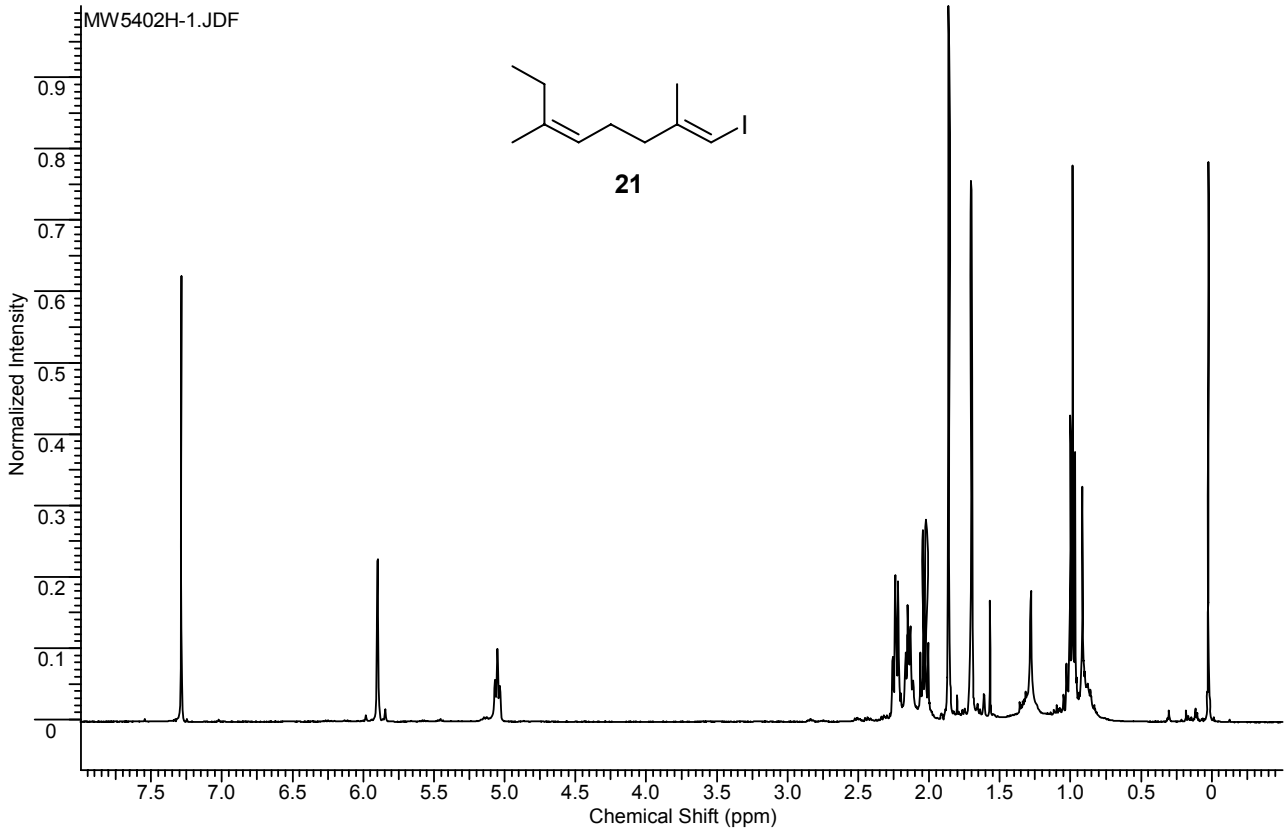

mw4628H-3.jdf
TMS
I
19
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


gd3832C-1.jdf
TMS
I
19
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

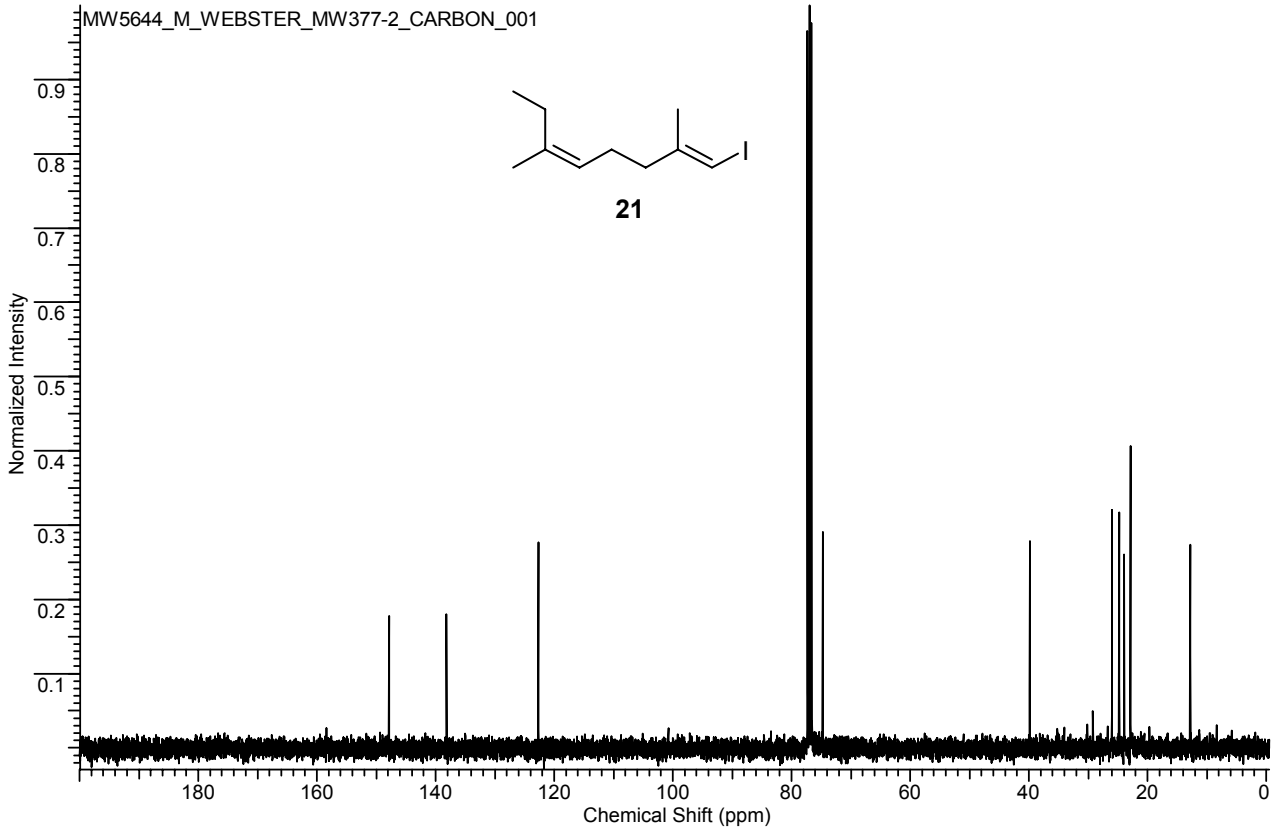

MW44405H-3.JDF
TMS
20
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


gd0114C-3.jdf
TMS
Normalized Intensity
Chemical Shift (ppm)

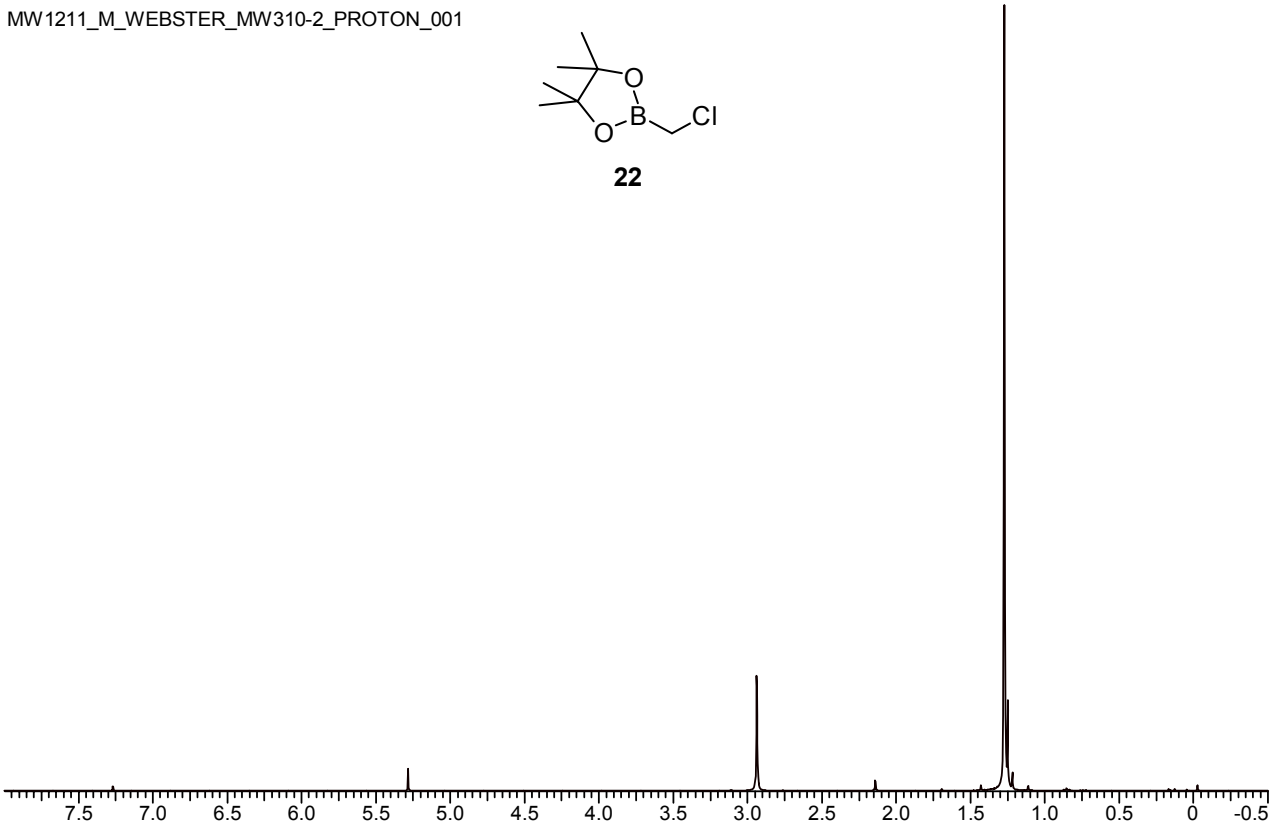
20


MW5402H-1.JDF
I
Normalized Intensity
Chemical Shift (ppm)

21

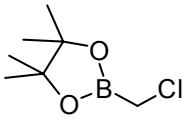

MW5644_M_WEBSTER_MW377-2_CARBON_001
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
I

21


MW1211_M_WEBSTER_MW310-2_PROTON_001
O
B
O
Cl
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5

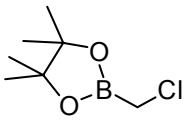
22

MW1214_MW310-2_DRIED_CARBON_001



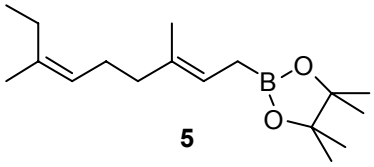
22

MW1214_MW310-2_DRIED_S2PUL_001



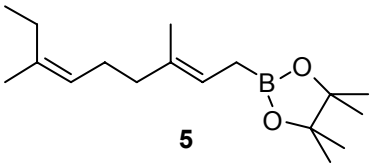
22

MW47918_MWEBSTER_MW399_2H-3.JDF

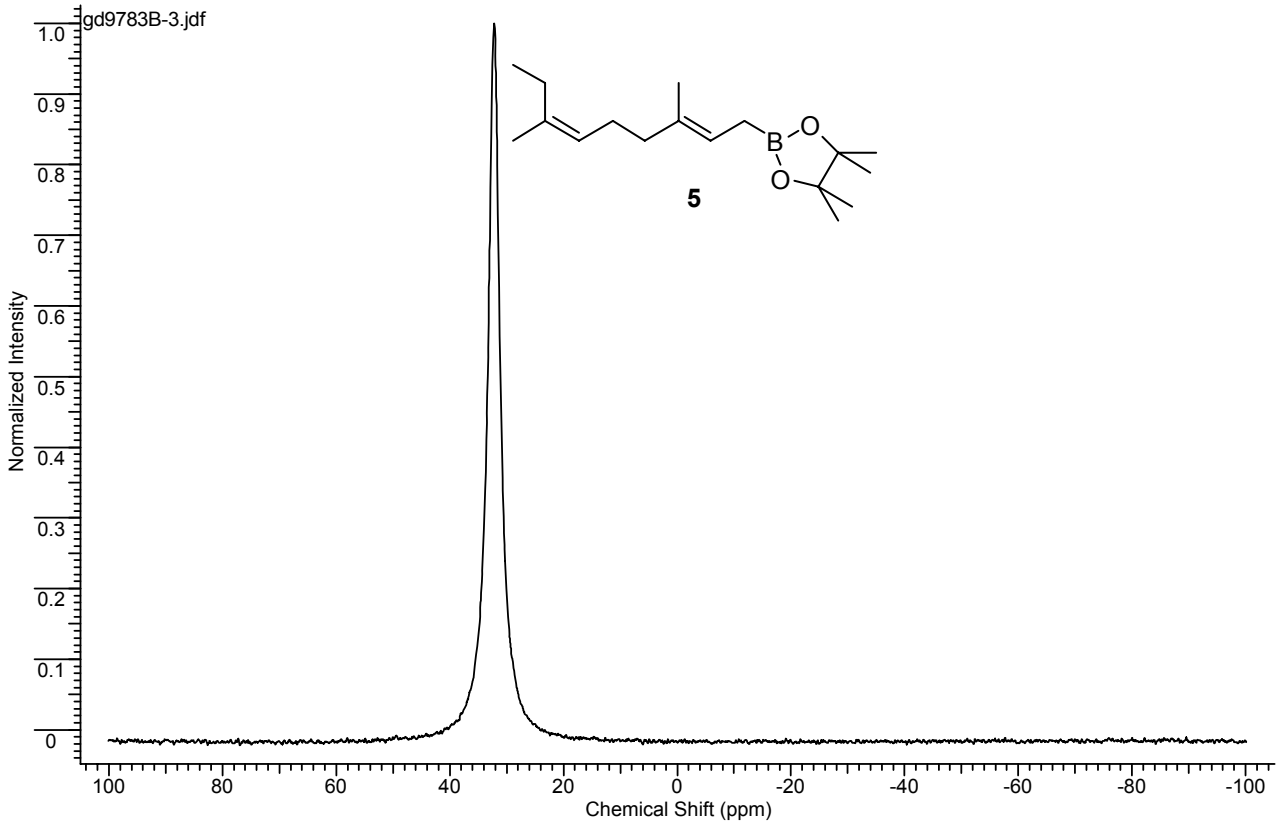


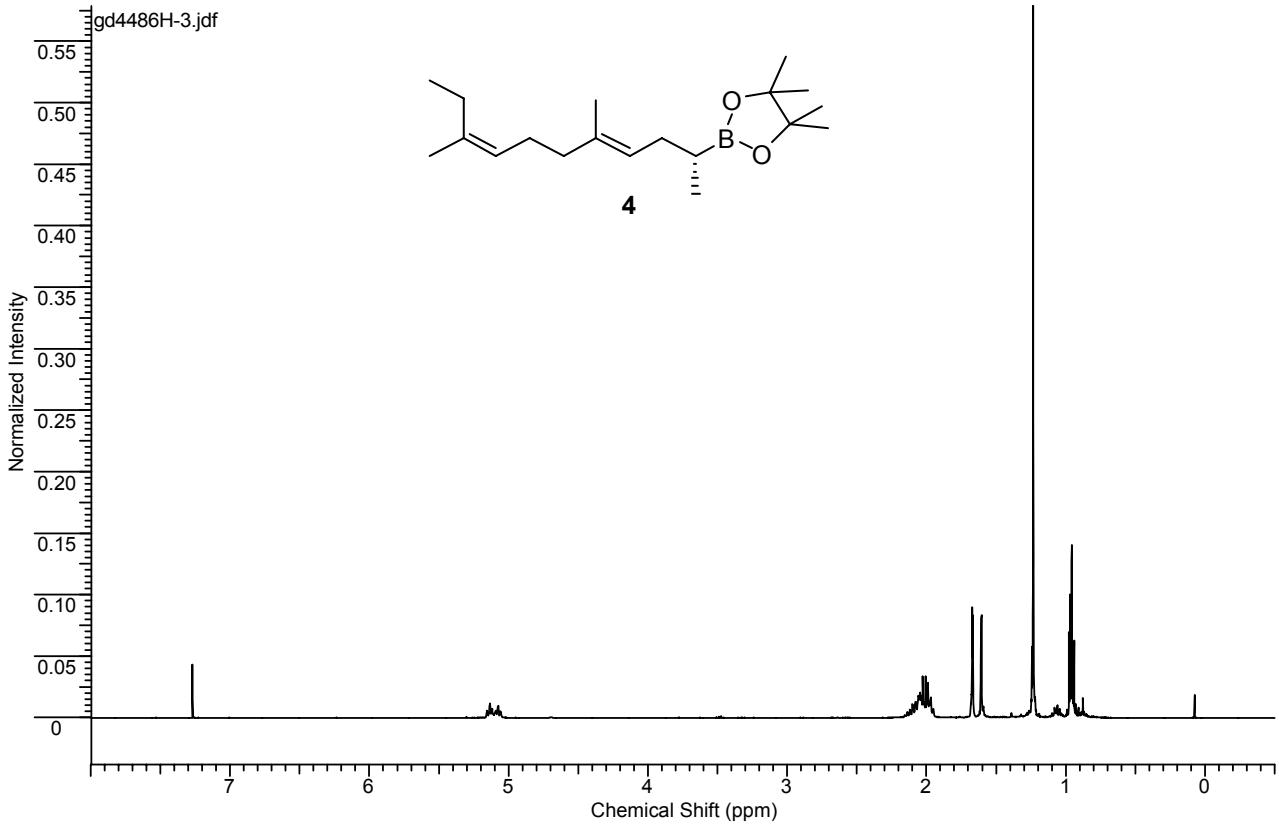
5

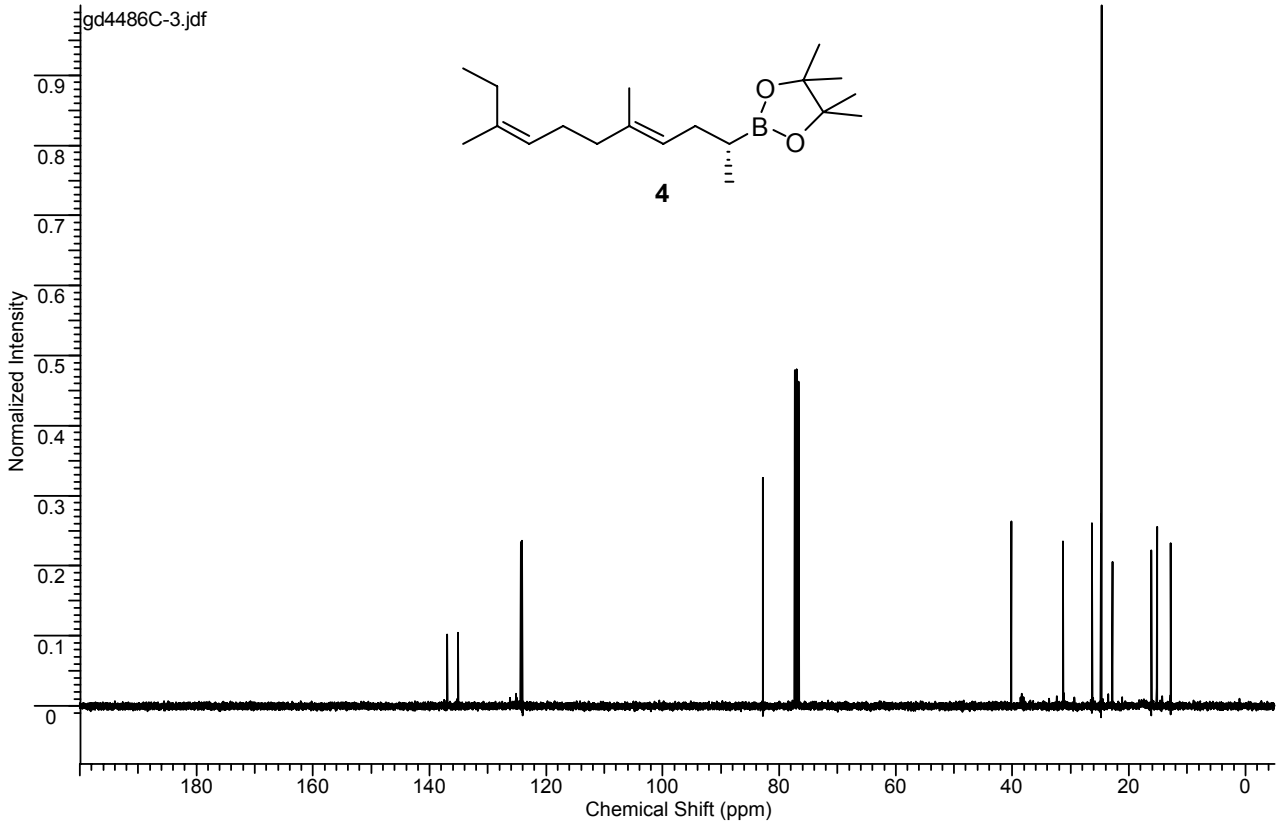
gd4456C-3.jdf

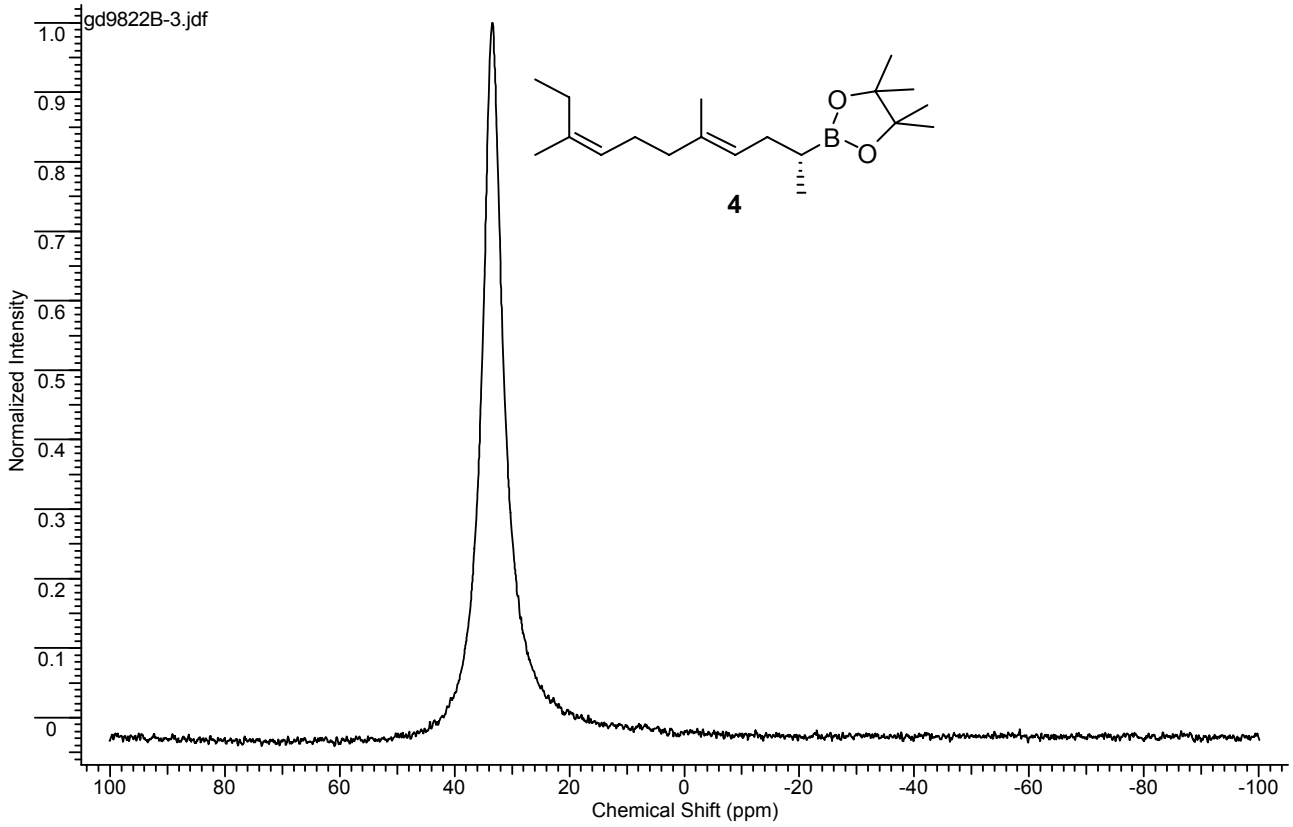


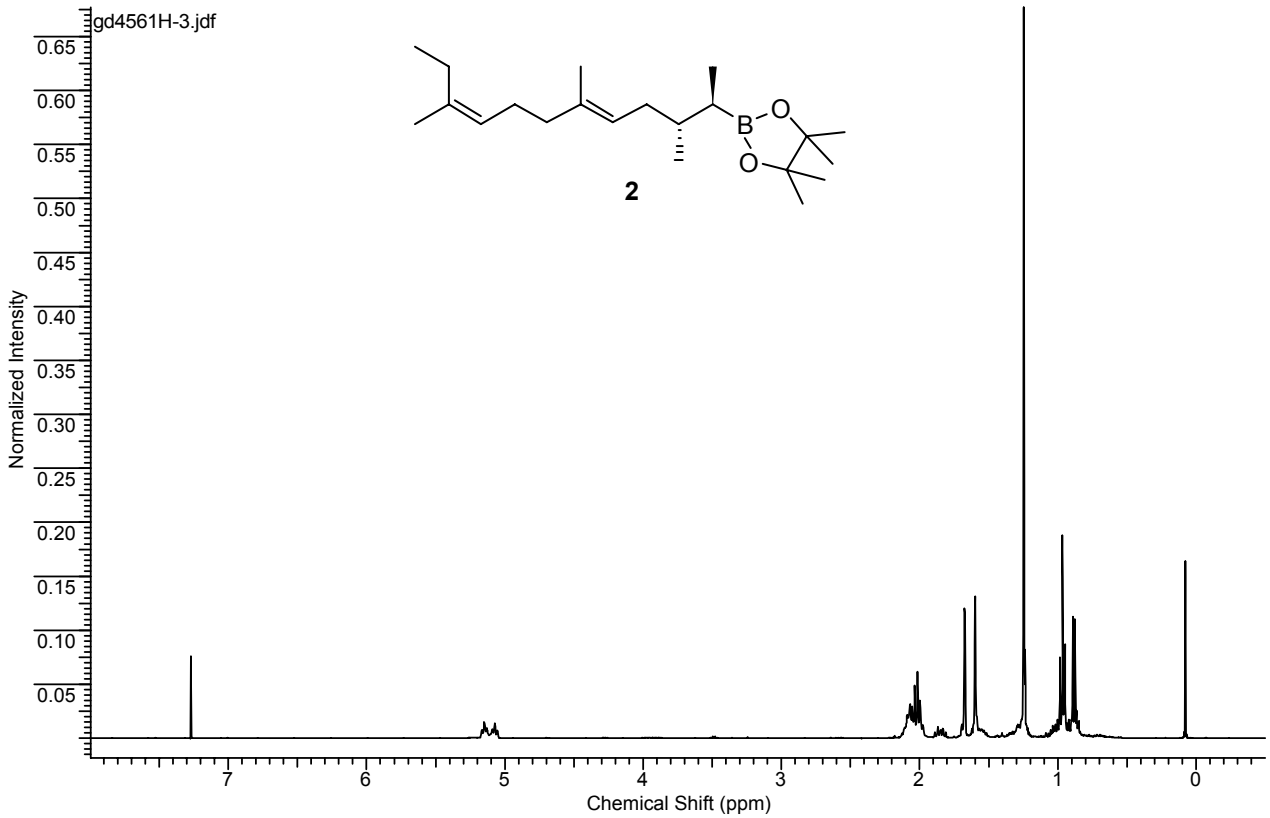
5


gd9783B-3.jdf
Normalized Intensity
Chemical Shift (ppm)
5

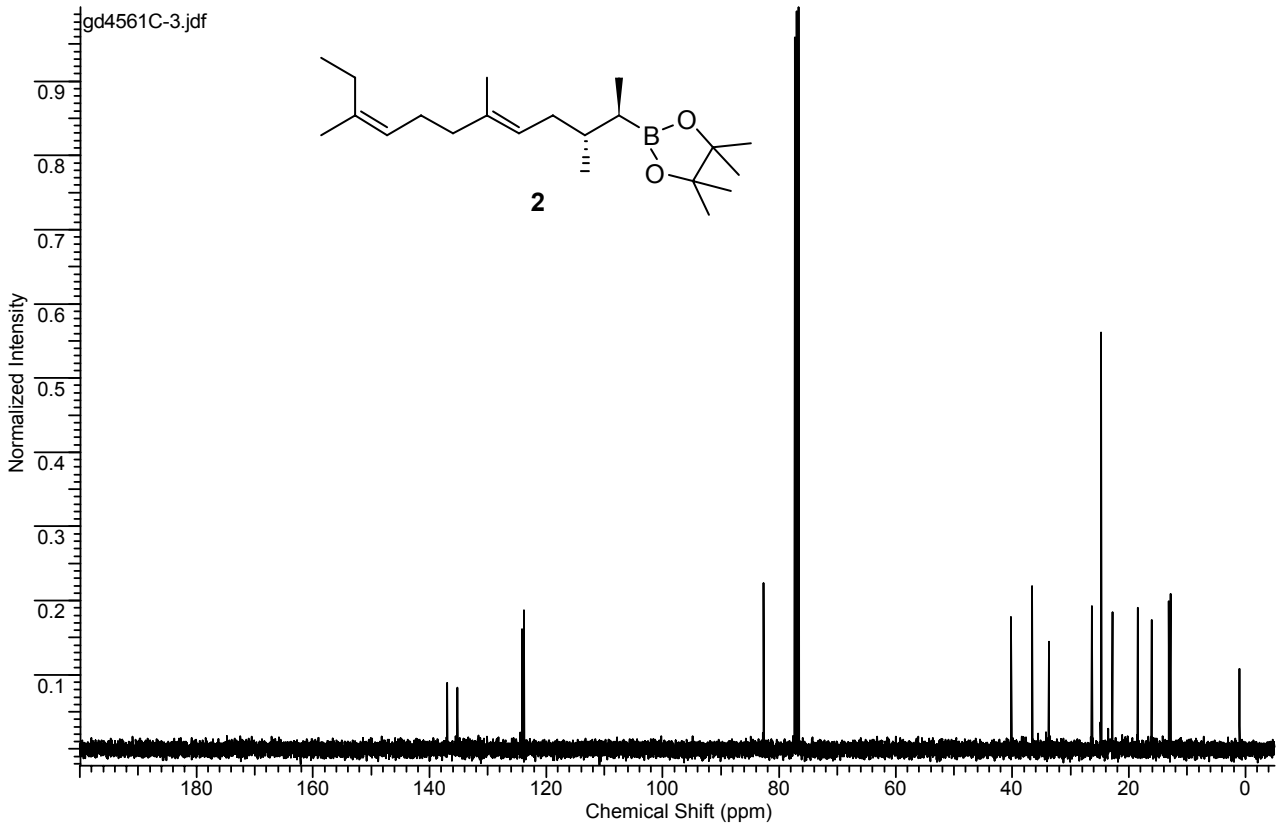

gd4486H-3.jdf
Normalized Intensity
Chemical Shift (ppm)
4


gd4486C-3.jdf
Normalized Intensity
Chemical Shift (ppm)
4

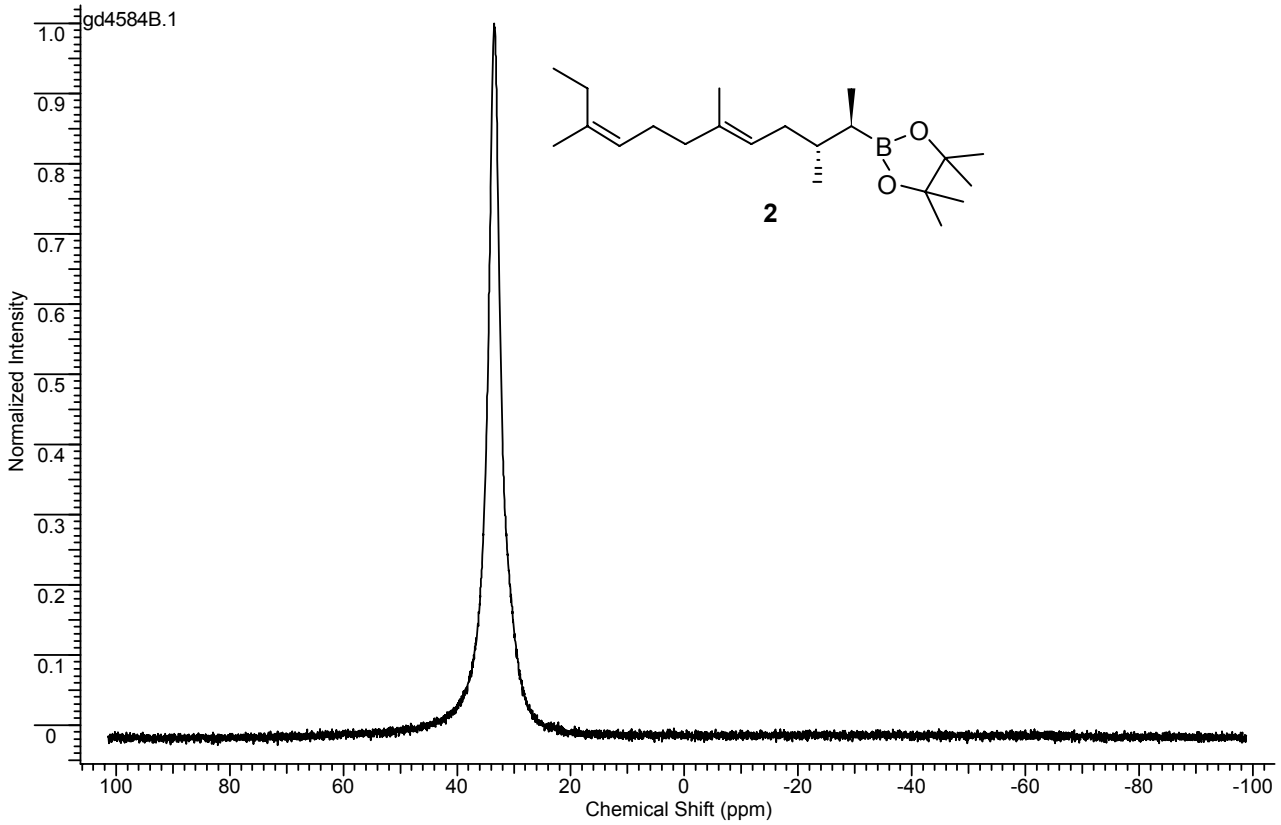

gd9822B-3.jdf
Normalized Intensity
Chemical Shift (ppm)
4


gd4561H-3.jdf
Normalized Intensity
Chemical Shift (ppm)
B
O
O

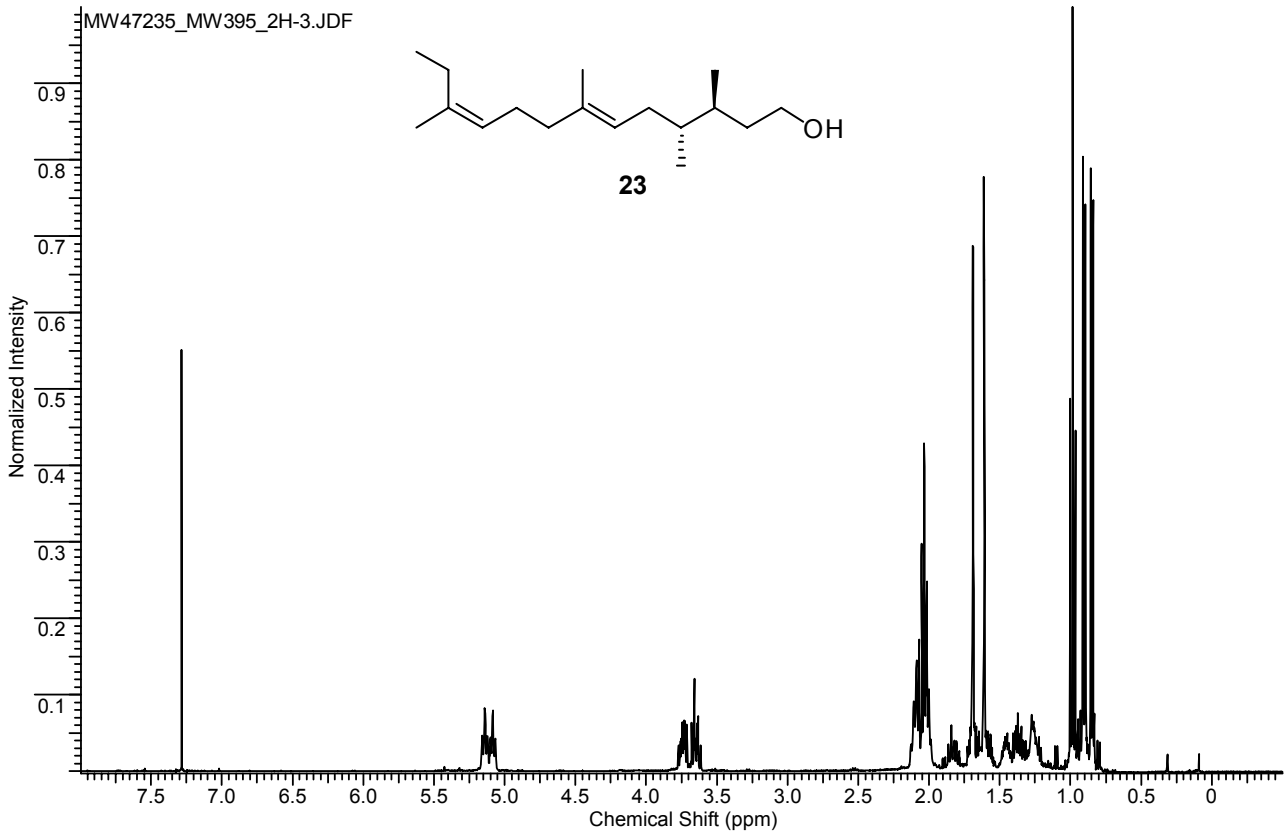
2


gd4561C-3.jdf
Normalized Intensity
Chemical Shift (ppm)
B
O
O

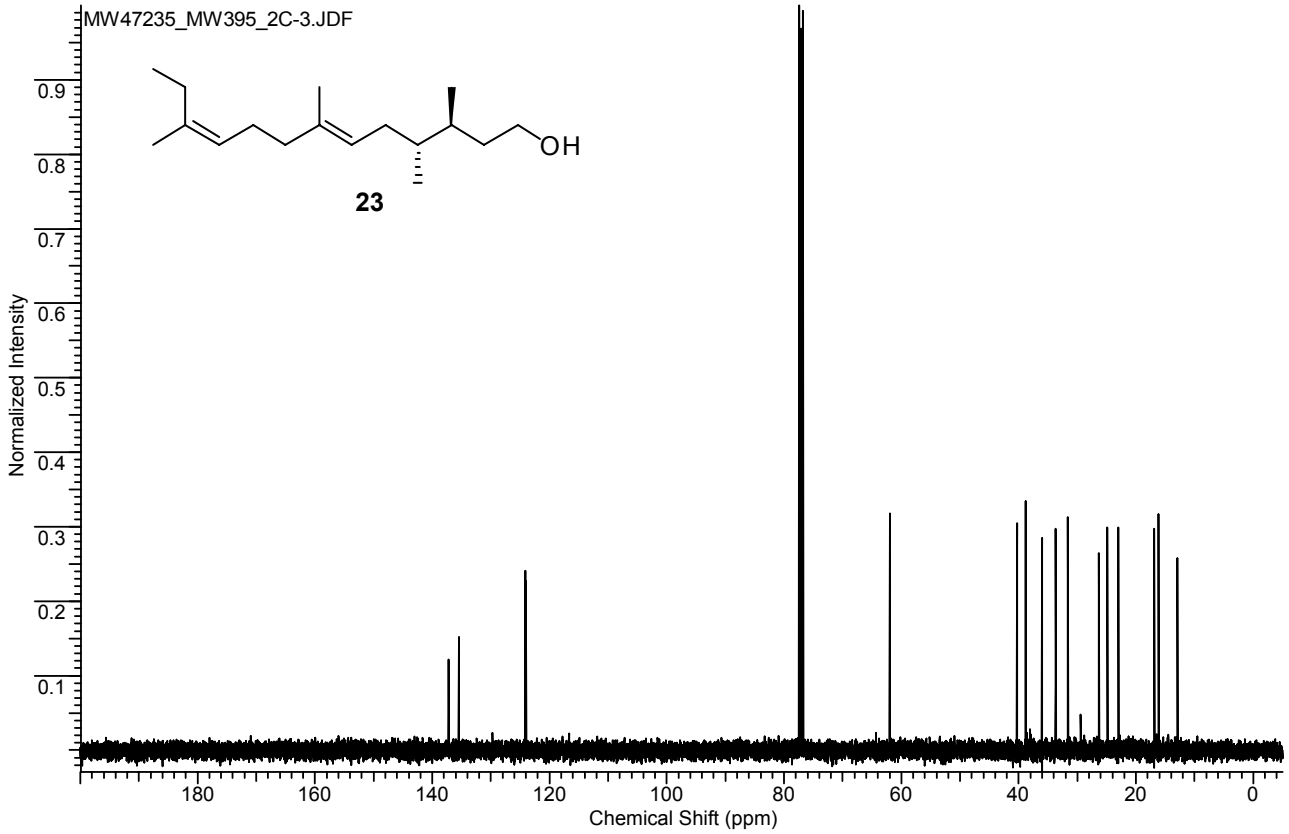
2

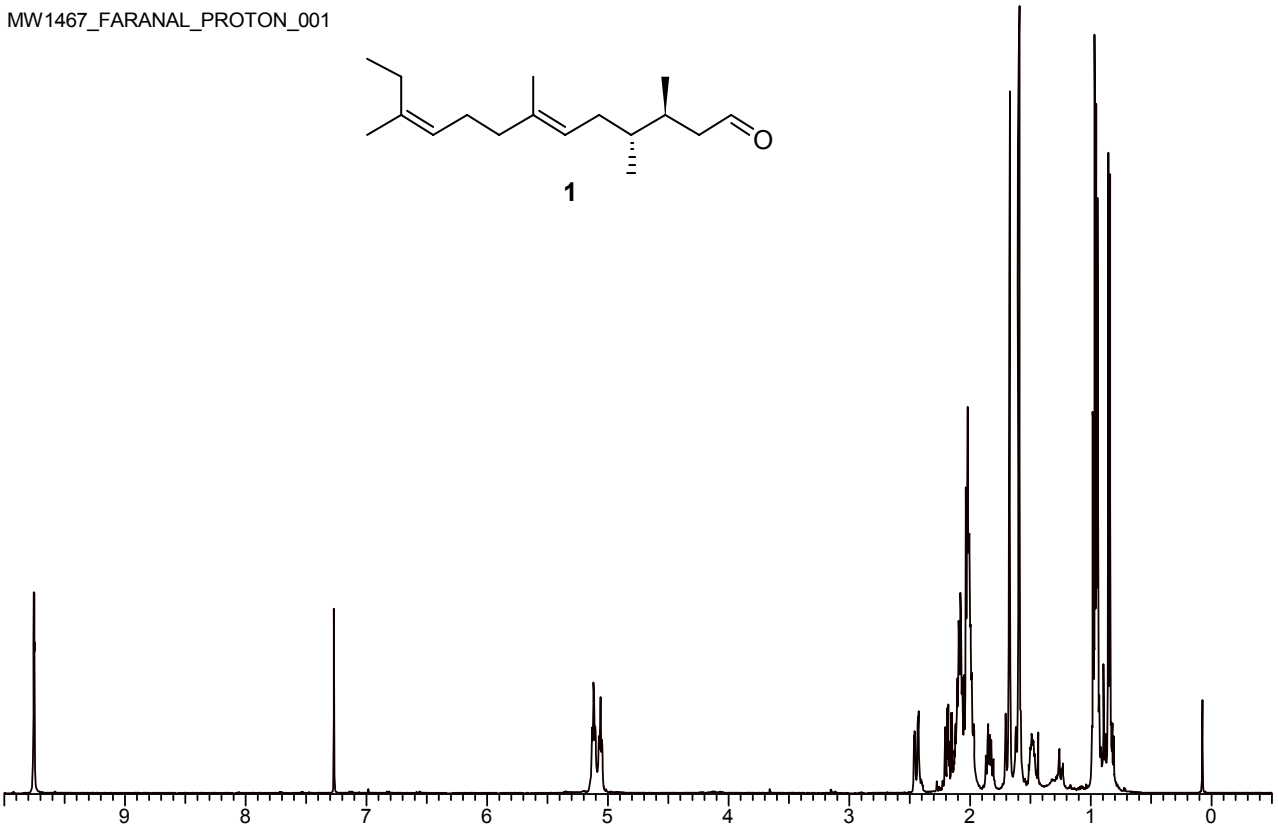

gd4584B.1
Normalized Intensity
Chemical Shift (ppm)
B
O
O

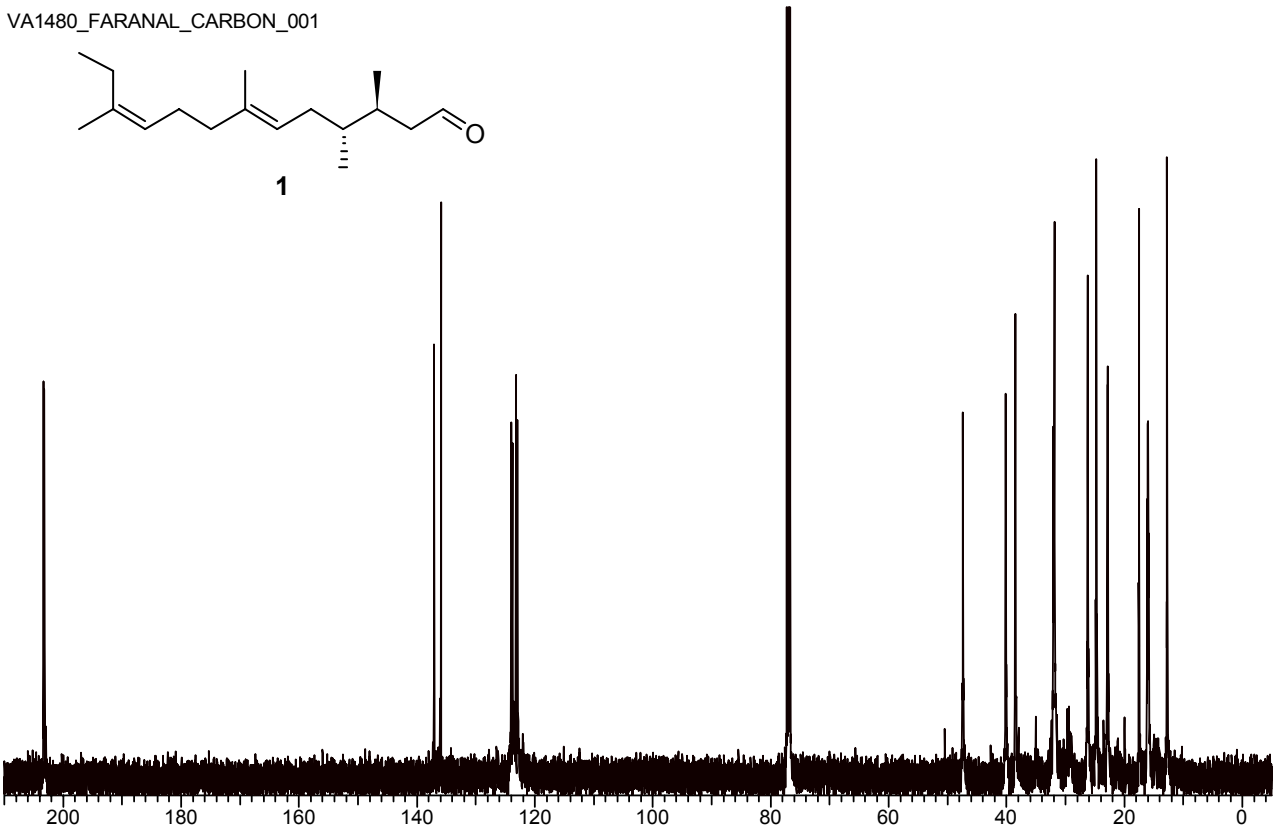
2


MW47235_MW395_2H-3.JDF
Normalized Intensity
Chemical Shift (ppm)
OH

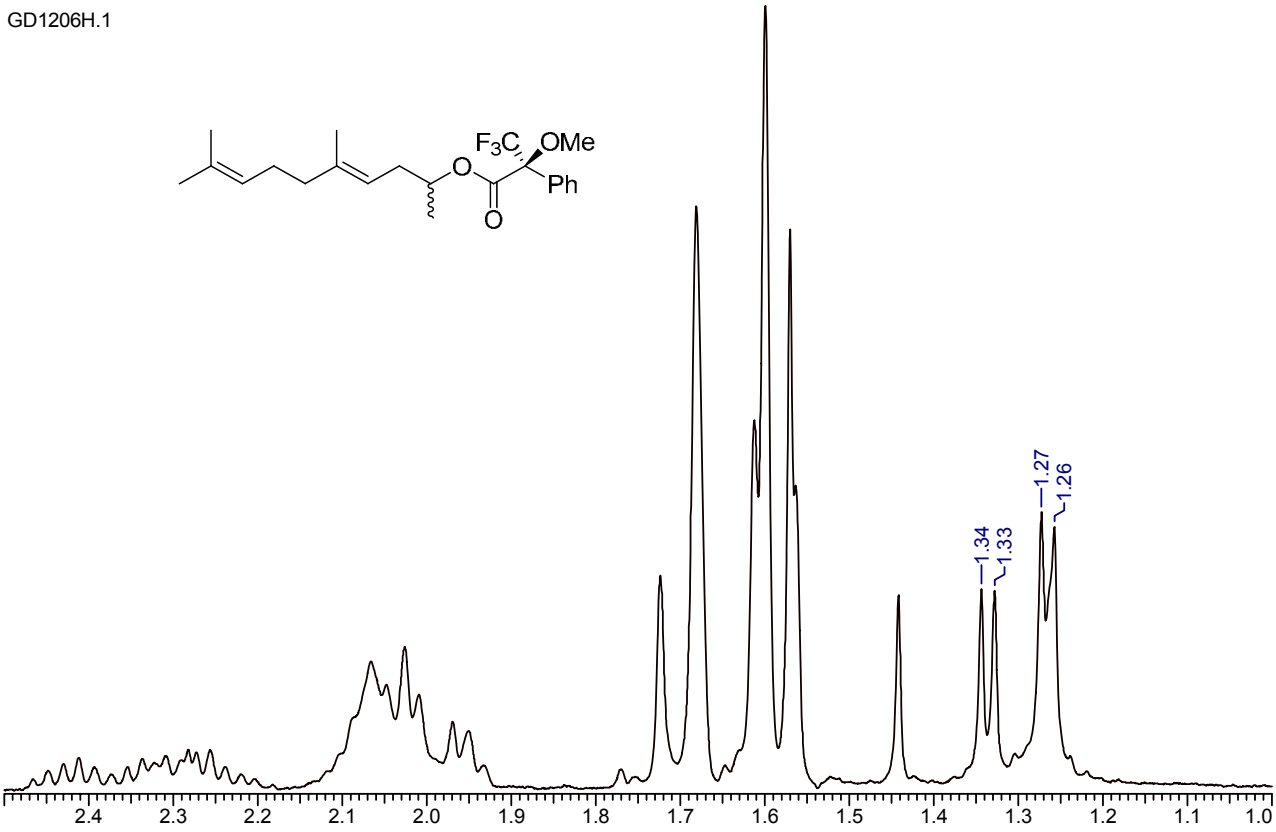
23

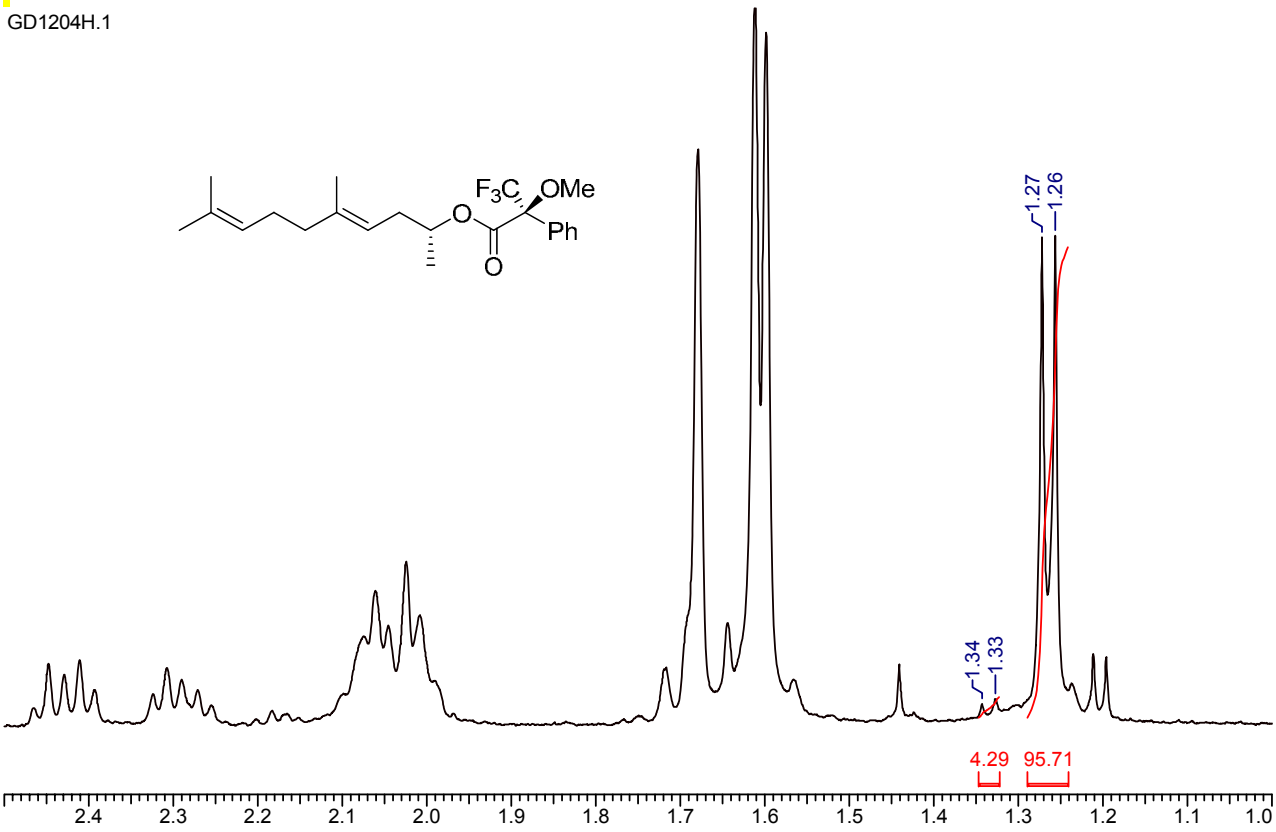

MW47235_MW395_2C-3.JDF
OH
23
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


MW1467_FARANAL_PROTON_001
O
1
9
8
7
6
5
4
3
2
1
0


VA1480_FARANAL_CARBON_001
O
1
200
180
160
140
120
100
80
60
40
20
0

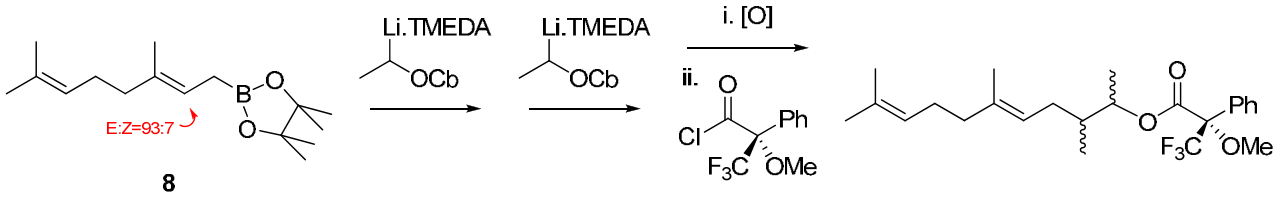
4. ^{1}H spectra of Mosher's esters for the determination of the e.r. of the first homologation, geraniol-derived model synthesis:



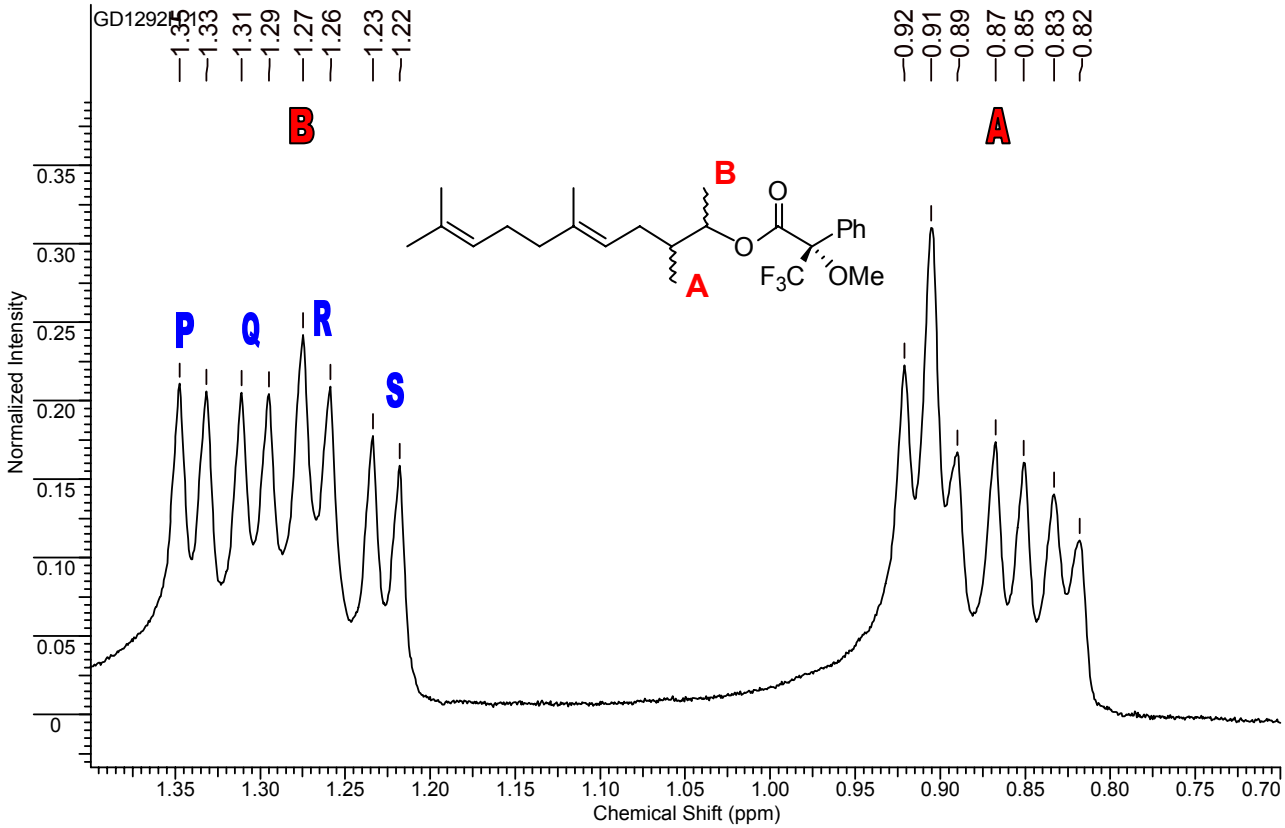


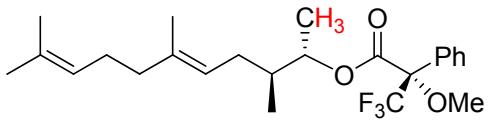
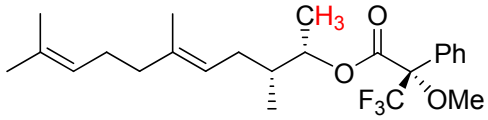
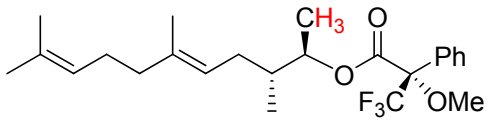
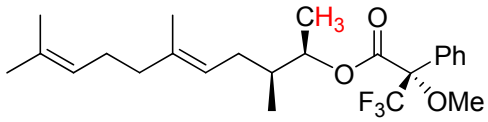
5. ^{1}H spectra of Mosher's esters for the determination of the e.r. and d.r. of the second homologation; geraniol-derived model synthesis:

The homologations were first carried out using TMEDA in place of (-)-sparteine. This was followed by oxidation and synthesis of the Mosher esters.



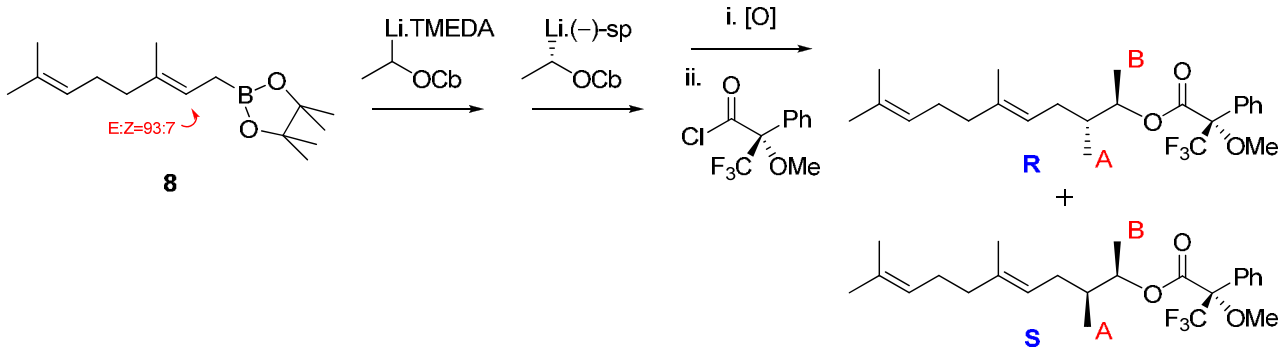
The doublets (corresponding to CH_3's **A** & **B**) for each diastereoisomer could be seen by ^{1}H-NMR ($CDCl_3$, 400 MHz). Diastereomers labelled **P**, **Q**, **R** and **S** (see below).

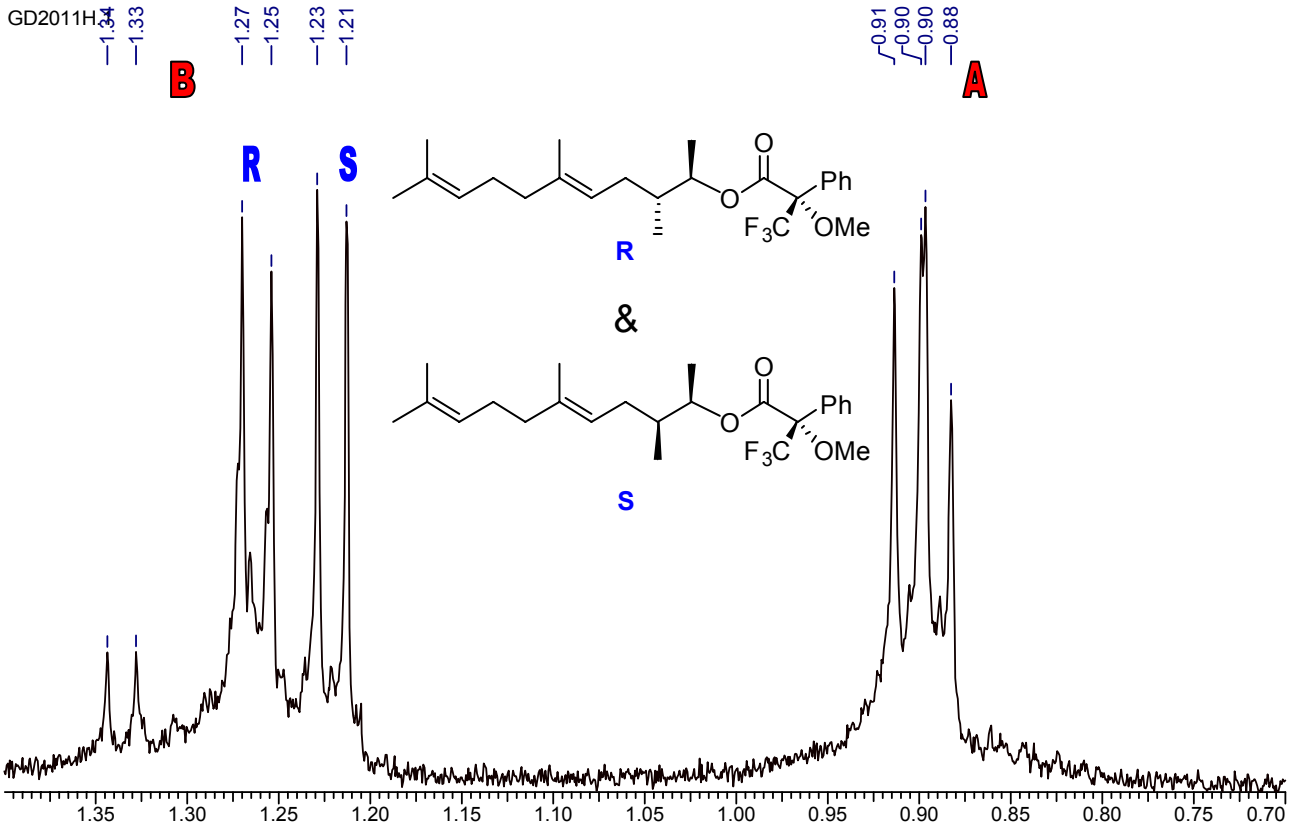


Diastereoisomer	Chemical Shift of indicated methyl group (ppm)	
P	1.34	
Q	1.30	
R	1.26	
S	1.22	

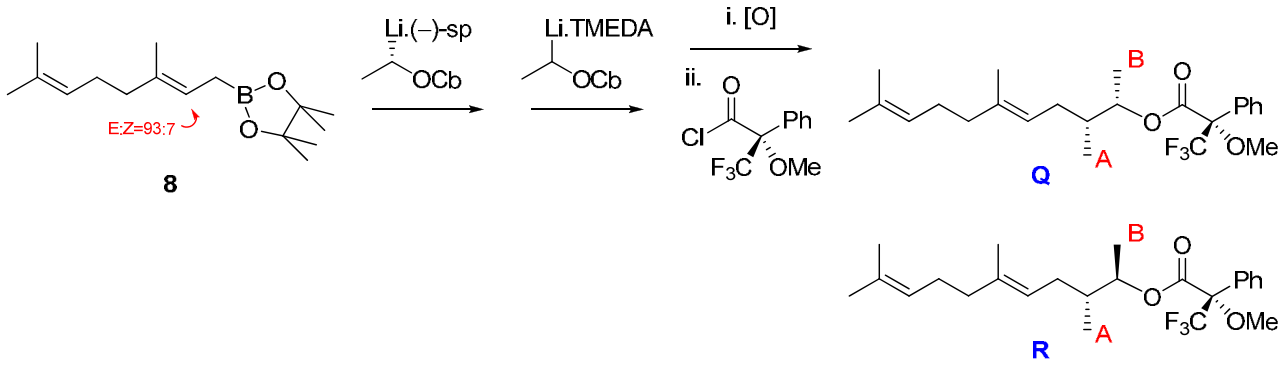
The method of determination of which set of peaks correspond to which diastereomers is given below.

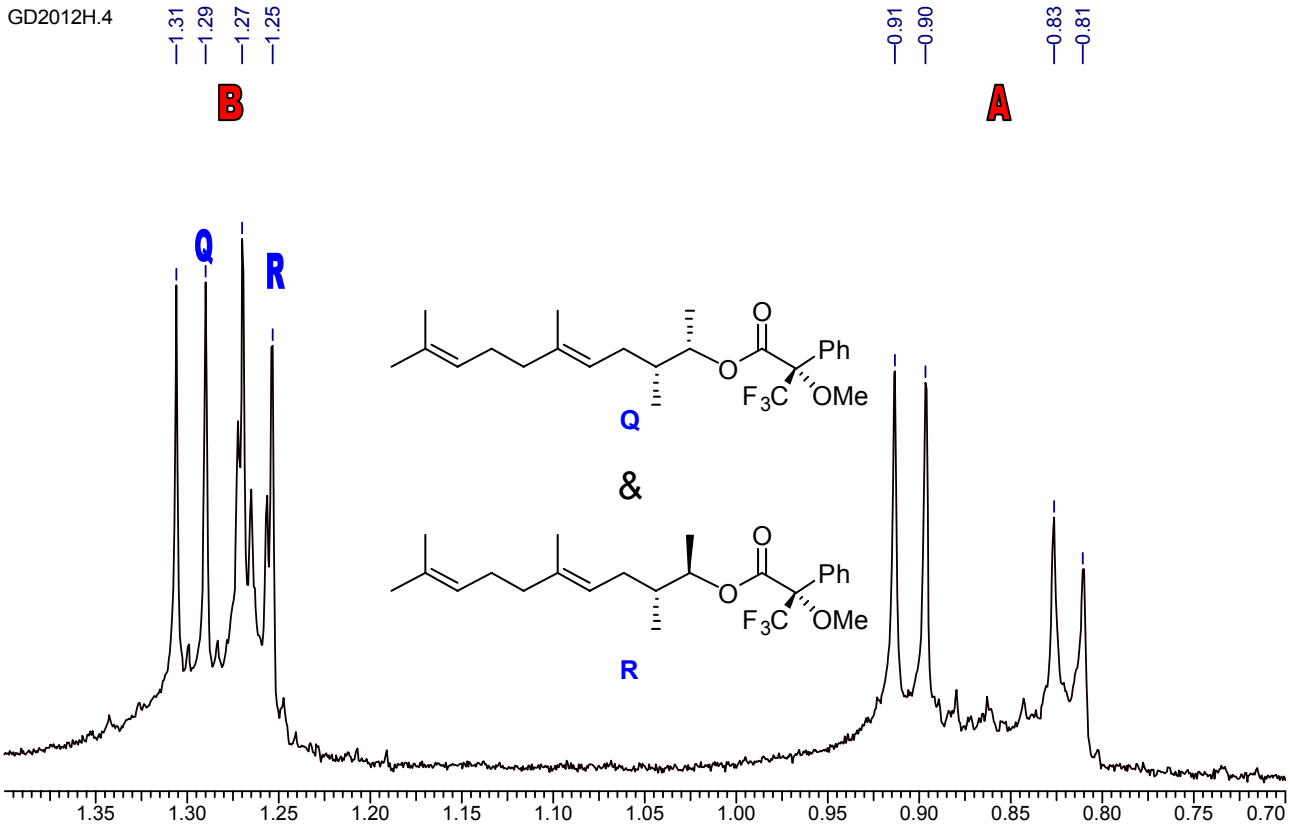
The first homologation was carried out using TMEDA and the second using (-)-sparteine. This was followed by oxidation and synthesis of the Mosher esters.



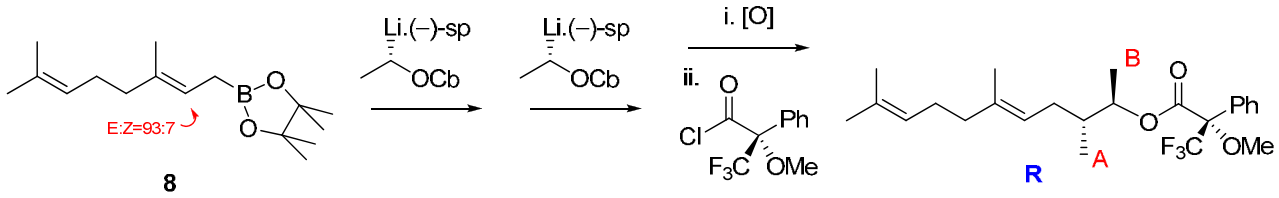


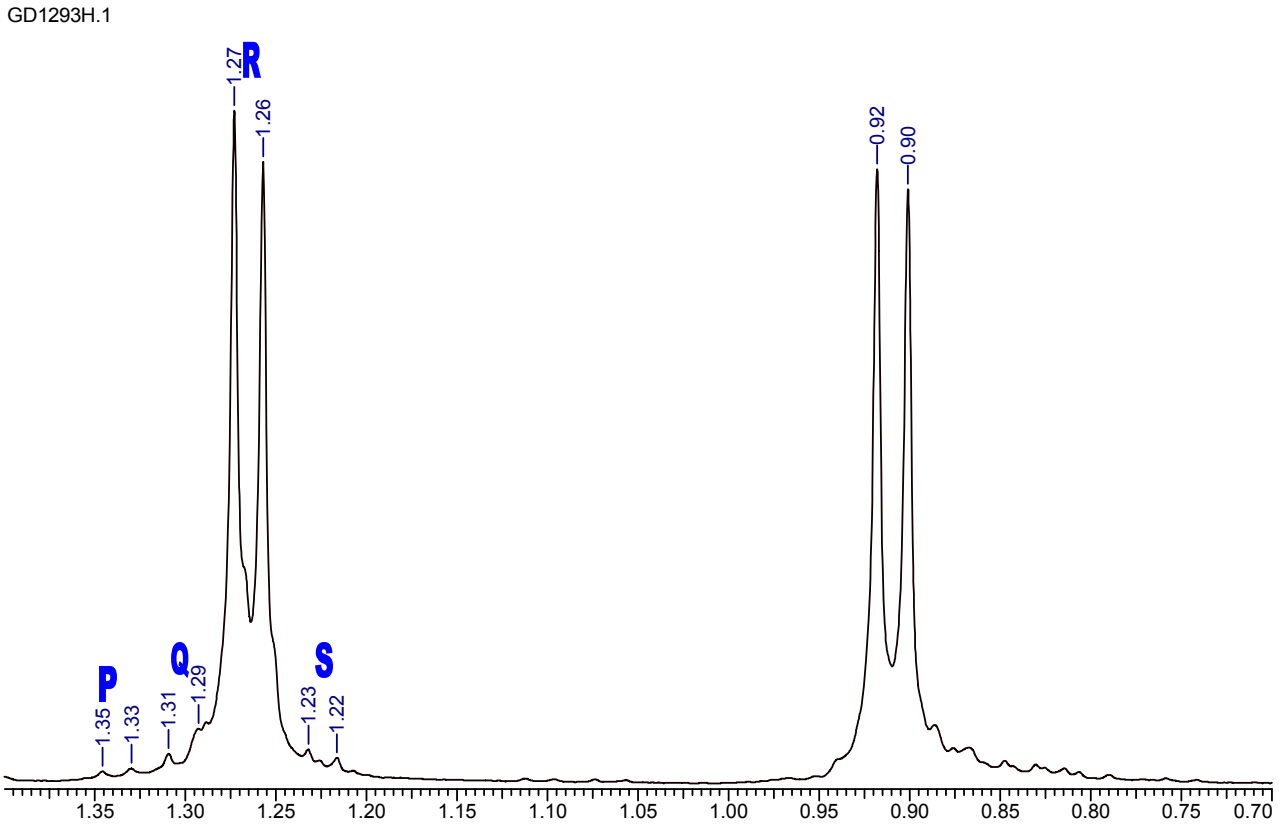
The first homologation was carried out using (-)-sparteine and the second using TMEDA. This was followed by oxidation and synthesis of the Mosher esters.





The homologations were both carried out using (-)-sparteine.



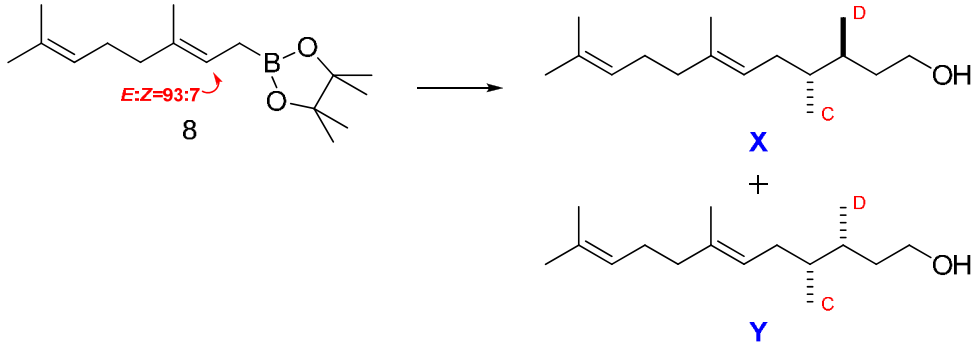


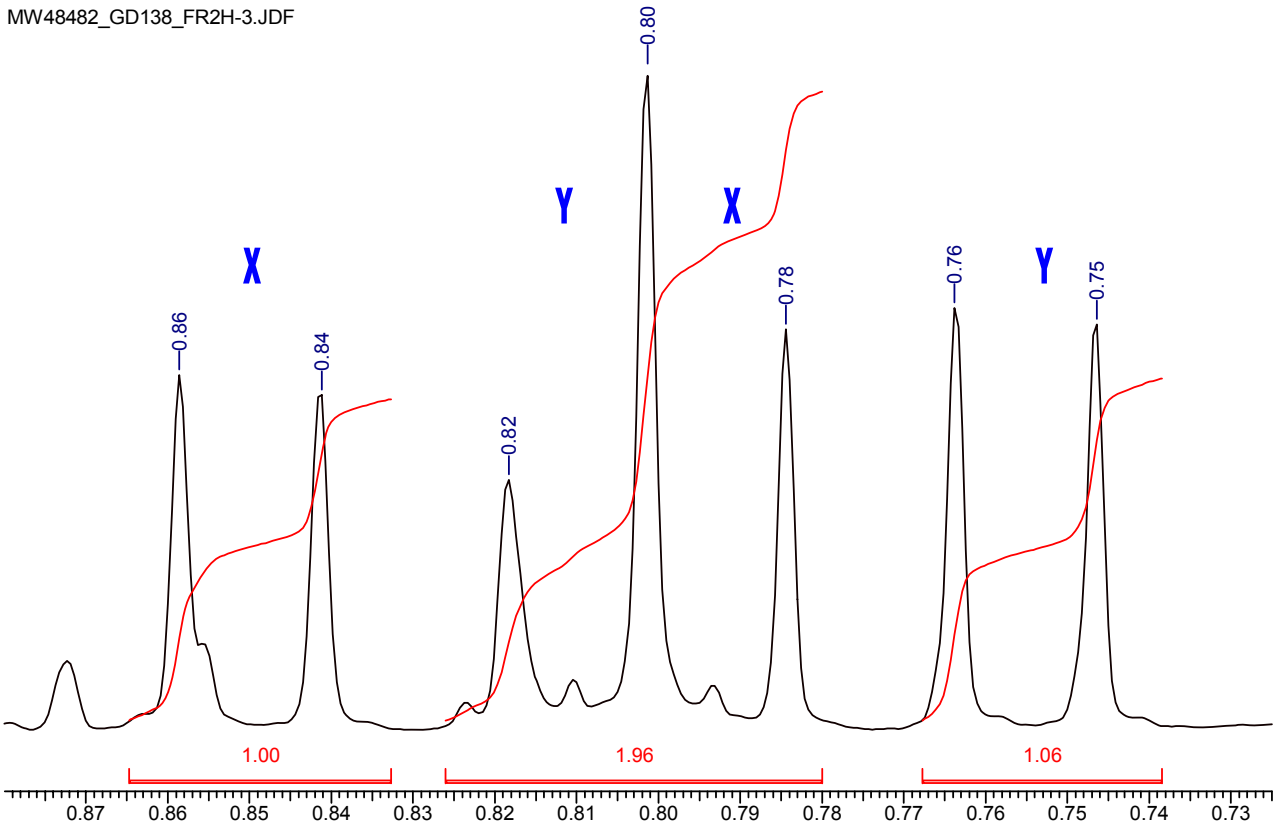
e.r. = ratio of **R**:**P** = >98:2.

d.r. = ratio of (**R**+**P**):(**Q**+**S**) = 94:6.

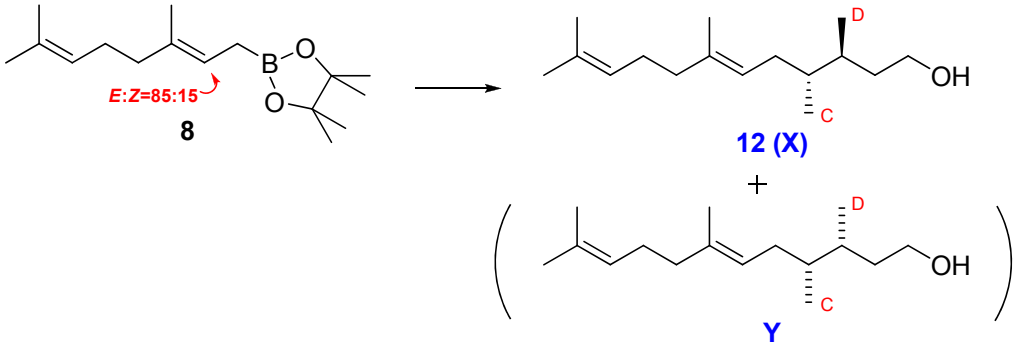
6. ^{1}H spectra for determination of the d.r. of one-pot processes

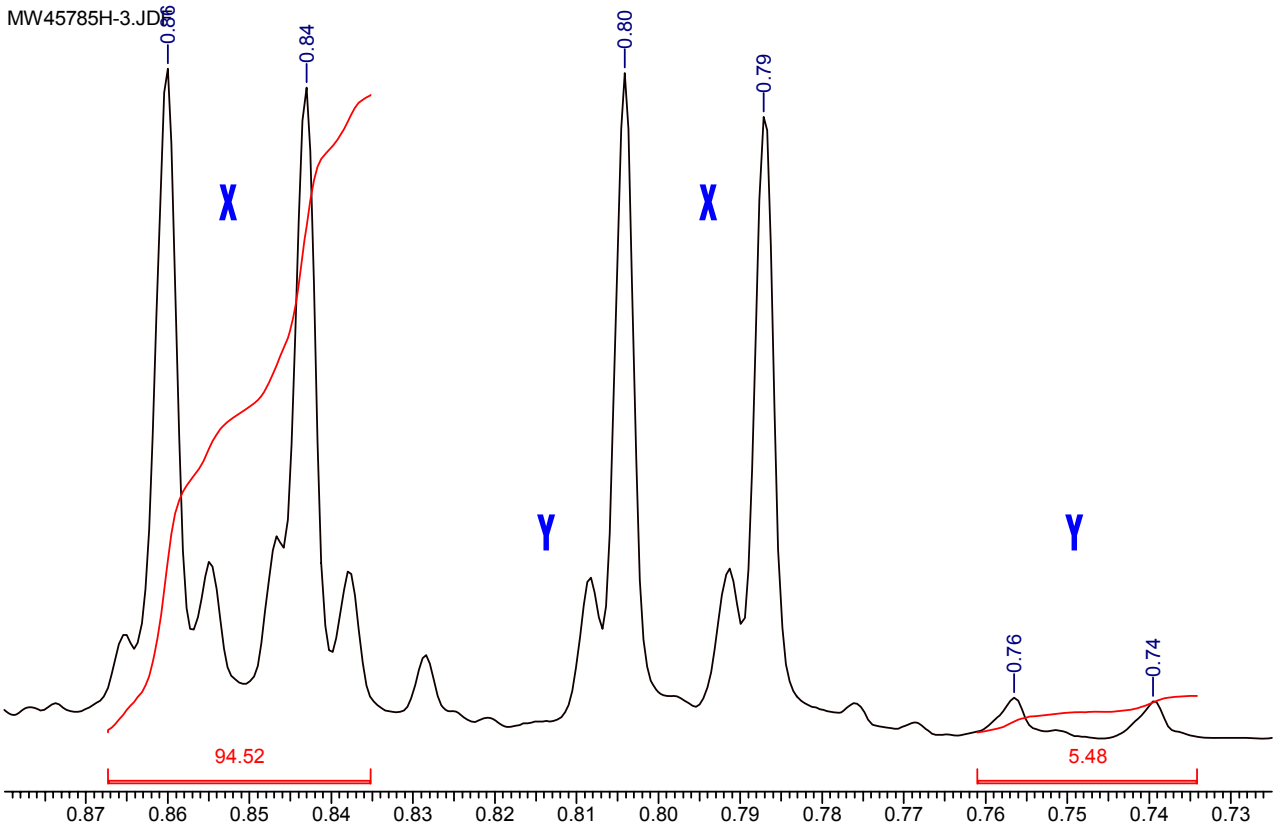
The one-pot synthesis of **12** (geraniol-derived model system) was carried out racemically using TMEDA in place of sparteine. The doublets corresponding to methyl groups C and D (labelled below) of both diastereoisomers could be identified by ^{1}H-NMR (400 MHz, C_6D_6).



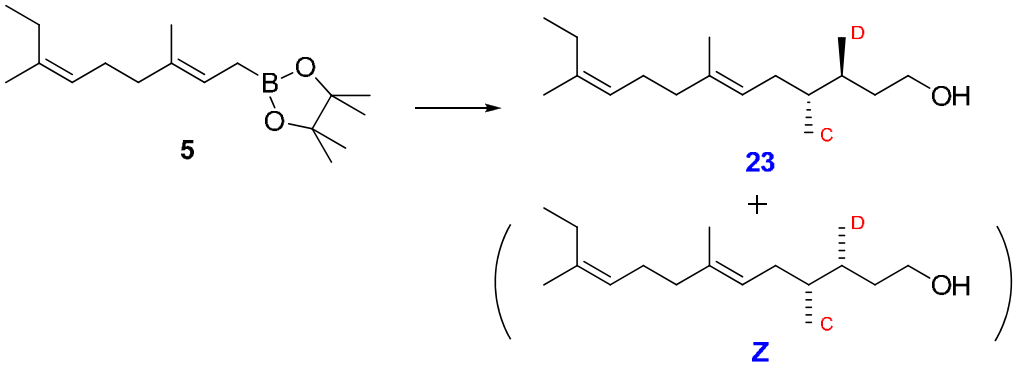


The one-pot stereocontrolled synthesis of **12** using (–)-sparteine was carried out as described in the experimental procedures section. Analysis of ^{1}H-NMR (as above) allowed for calculation of d.r. (94:6). N.B. Starting boronate **8** in this example was 85:15 *E*:*Z*.

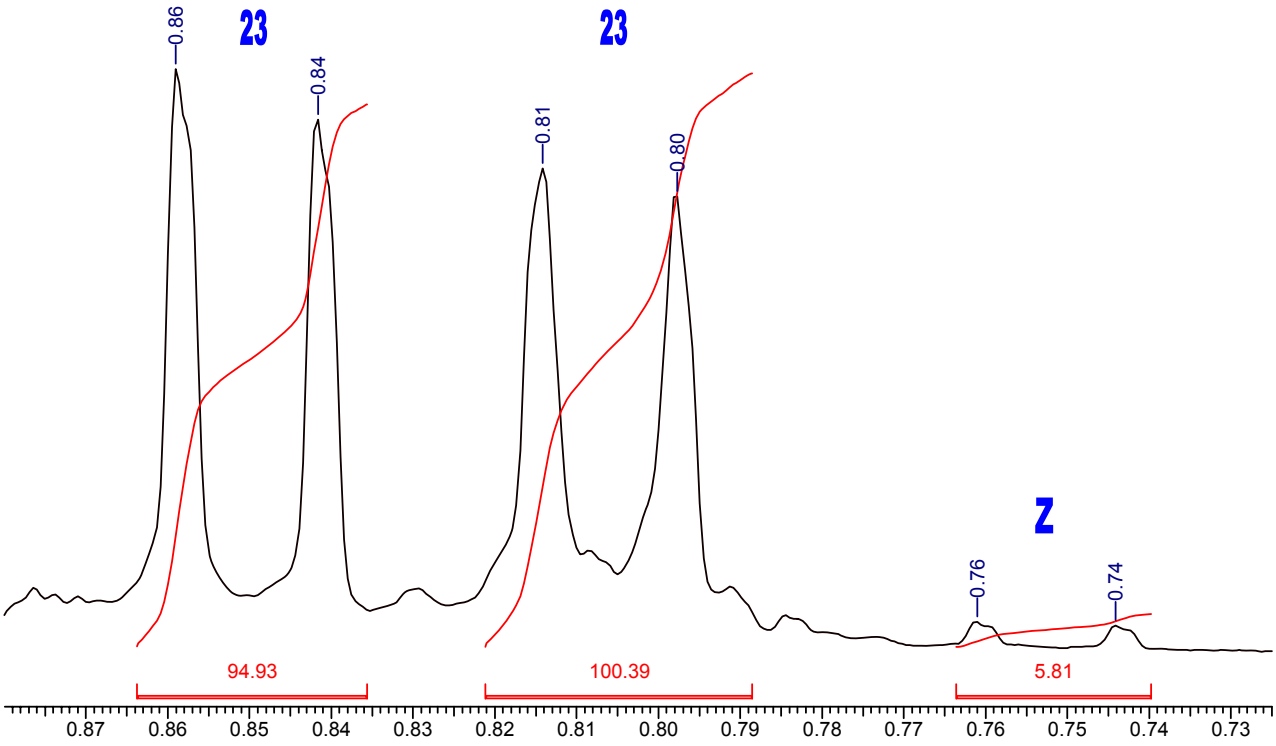




By analogy the d.r. of **23** from the one pot sequence toward (+)-faranal (**1**) was 94:6 (**23**:**Z**).



MW48406_MWEBSTER_MW395_2_BENZENEH-3.JDF



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